AN ANALYSIS OF FACTORS INFLUENCING THE RELIABILITY OF RETRIEVABLE STORAGE CANISTERS FOR CONTAINMENT OF SOLID HIGH-LEVEL RADIOACTIVE WASTE

by

W. J. Mecham, W. B. Seefeldt,
and M. J. Steindler

U of C-AUA-USERDA

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

ANL-76-82

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois   60439

AN ANALYSIS OF FACTORS INFLUENCING THE
RELIABILITY OF RETRIEVABLE STORAGE CANISTERS FOR
CONTAINMENT OF SOLID HIGH-LEVEL RADIOACTIVE WASTE

by

W. J. Mecham, W. B. Seefeldt,
and M. J. Steindler

Chemical Engineering Division

August 1976

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

AN ANALYSIS OF FACTORS INFLUENCING THE RELIABILITY OF RETRIEVABLE STORAGE CANISTERS FOR CONTAINMENT OF SOLID HIGH-LEVEL RADIOACTIVE WASTE

by

W. J. Mecham, W. B. Seefeldt
and M. J. Steindler

ABSTRACT

The reliability of stainless steel type 304L canisters for the containment of solidified high-level radioactive wastes in the glass and calcine forms was studied. A reference system, drawn largely from information furnished by Battelle Northwest Laboratories and Atlantic Richfield Hanford Company is described. Operations include filling the canister with the appropriate waste form, interim storage at a reprocessing plant, shipment in water to a Retrievable Surface Storage Facility (RSSF), interim storage at the RSSF, and shipment to a final disposal facility.

The properties of stainless steel type 304L, fission product oxides, calcine, and glass were reviewed, and mechanisms of corrosion were identified and studied. The modes of corrosion important for reliability were stress-corrosion cracking, internal pressurization of the canister by residual impurities present, intergranular attack at the waste-canister interface, and potential local effects due to migration of fission products.

The key role of temperature control throughout canister lifetime is considered, together with interactive effects.

Methods of ameliorating adverse effects and ensuring high reliability are identified and described.

Conclusions and recommendations are presented.

SUMMARY

The basic question addressed in this study is the reliability of waste canisters in engineered storage of radioactive wastes from commercial nuclear power reactors. In this study, reliability was taken to be the *reliability of retrievable storage by the current state of technology* consistent with the conceptual designs of the Retrievable Surface Storage Facility (RSSF) by ARHCO, where the reference storage period is 100 yr. Where there was design latitude of the RSSF, certain state of the art reference design specifications were set by the reviewers to establish a concrete system for the study of reliability.

The basic waste package stored in the RSSF is a cylindrical metal canister, into which concentrated fission product waste is charged as dry solid oxide-- either granular (calcine) or as a vitrified mass (by use of silicate additions to form glass). In this study, reliability was defined narrowly to mean the inherent ability of the canister to remain intact for the period of storage. If the canister remains intact, the waste is completely isolated from the human environment and no leaching or other dispersion practices can take place.

We confined our attention to the range of conditions for which inherent reliability is expected and did not evaluate the effects of nonreliability, *i.e.*, the hazardous consequences of failure of the canister to provide effective containment. Our focus on realistic practical operation led us to confine our attention to only those abnormal and accident situations that were considered in our judgment to be reasonable departures from normal conditions and therefore representative of the inherent reliability of the storage concept.

Since safety is, by definition, evaluated in terms of the risk involved in the consequences of nonreliability of containment, we did not directly address safety except to indicate that radioactivity released in the event of canister failure is subject to confinement by secondary containment features of the facility and to control by monitoring and remedial-action features of the system.

Our aim was to evaluate reliability in terms of current reliability methodology, which has the form of quantitative systems analysis. As in all engineering concepts, there is a trade-off (explicit or implicit) between cost and reliability. The specifics of the trade-off are, in fact, the definition of current technology. We found that the promise of inherent reliability of waste storage is good in terms of basic feasibility, but that the system design lacks the sort of specificity and supporting performance data needed to establish reliability quantitatively and in terms clearly convincing to outside reviewers. We see our limited study as aiming to further define the reliability of the system, and we have stated the ways we believe further effort is required.

We initiated our study as an examination of the chemical nature of the materials involved: the solid waste, the canister, and the coolant (in the storage environment) for the reference system concept.

Canister metals can be chosen from common alloys having strength and corrosion resistance to air- and water-cooling environments. Corrosion was

considered in detail for 304L an austenitic stainless steel that would have good corrosion resistance, provided that certain limits are placed on temperature, stress, and the chemical environment of the canister. For air-cooling environments, chemical factors are not critical for corrosion control and resistance to corrosion is high at surface temperatures below the sensitization temperature of about 430°C. With water cooling, all alloys are subject to some degree of corrosive attack at elevated temperatures depending on the various properties of the water, especially the amount of oxygen or halide present and the acid or caustic content. In addition, 304L that is highly stressed may be subject to stress corrosion cracking in water containing traces of certain materials such as chlorides. Conditions of control of water properties for reliability were considered in detail, but the absence of data on the corrosion resistance for long periods of exposure prevented optimum conditions being established for reliability on an evidential basis. At present, water cooling requires stringent state-of-the-art controls for reliable service of SS 304L, including control of the composition of water and of those conditions associated with filling of the canister which would expose the canister to temperatures over 430°C or would develop internal high stress levels. The latter condition requires special precautions if the solid waste is solidified (cast) in the canister as a glass.

We found that, for a solid fission-product waste formed by calcination, the most important characteristic is the amount of residual nitrate, water, and halides. It is desirable that the final temperature of calcination be as high as 800°C in order to reduce the level of these residuals to that at which there is no potential of creating pressure during storage if overheating should take place.

When canister wall temperatures are below the melting point of the chemical phases present, no corrosive attack of the canister from the inside is expected for waste in either the oxide or glass form. For wall temperatures below 500°C, molten phases are not likely to be present. Assessment of the effects of overheating, $i.e.$, inadvertent exposure to abnormally high temperatures, would require more detailed study of the particular compositions and structures of solid waste products from particular solidification and treatment processes. In general, fission product elements in the solid oxide form are high-melting, thermally stable, and noncorrosive to typical alloys. Detailed behavior in long-term storage depends on temperature and on oxidation potential. If water, nitrate, and halogens are kept at low levels and the wall temperature is kept below the calcine melting point, overheating of the central mass of calcine would not be expected to threaten canister integrity. A similar situation exists for glass, except that solid glass has a potential for stressing the canister which must be considered in establishing controls.

A variety of canister designs, including fins, stress relief, and the use of double canister containment (overpack), are available to meet specific control requirements for service reliability. The overall assurance of reliability (and safety and economy) is a matter of establishing designs and operating conditions for (a) waste-solidification and treatment processes, (b) material chemical properties in storage conditions, and (c) systems engineering of the overall waste-management operations. Our study concentrated on material-chemistry aspects of the problem and arrived at detailed conclusions to improve reliability in terms of specific properties, designs, and controls applied to the reference waste-managements system.

1. INTRODUCTION

The Nuclear Regulatory Commission (NRC) and its predecessor, the Atomic Energy Commission (AEC) have established and published regulations related to the handling of high-level radioactive wastes generated in a nuclear fuel reprocessing facility. Appendix F of 10 CFR Part 50 limits the inventory of liquid high-level radioactive wastes at a reprocessing plant to that produced in the prior five years. To meet this requirement, such liquid wastes must be converted to a dry solid in 5 yr or less and placed in a sealed container. Solidified waste (in a shipping cask that meets the requirements of 10 CFR Part 71) must be transferred to a Federal repository no later than ten years following separation of fission products from the irradiated fuel. The Federal repository will assume permanent custody upon receipt of these materials.

Thus, disposal of high-level radioactive fission-product waste material will not be permitted on any land other than that owned and controlled by the Federal Government.

The responsibility for handling, storing, and disposing of such wastes at the Federal repository in a manner that is not inimical to the public health and safety became an obligation of the AEC and its successor, ERDA. Under this policy, the Commission supported work at the Allied Chemical Corporation for the development of a fluidized-bed process for the conversion of liquid high-level wastes to a dry solid. In addition, the Commission supported significant and substantial work at the Pacific Northwest Laboratories (PNL) for the development of processes in which solidified high-level wastes are incorporated into stable matrices such as glasses.

The Commission supported a concept of interim retrievable storage of solidified high-level wastes for use until an acceptable method of permanent disposal is developed. Under this policy, the Atlantic Richfield Hanford Company (ARHCO) developed several alternative concepts of engineered retrievable surface storage. A prime design criterion for any such facility is an adequate level of engineered safeguards to ensure that public health and safety are not compromised.

The subject of the report is the reliability against failure of canisters that contain solidified waste forms.

2. BASIS OF ANALYSIS

2.1. Objective

The objective of the container reliability study is to identify as quantitatively as possible the reliability against failure and leakage of the canisters used to contain high-level wastes in each of two forms, glass and calcine. Reliability is to be related to the major system parameters and properties of the waste packages as defined for a conceptual design of a reference system for retrievable storage, including all of the life history of canisters and waste solids that influence containment reliability.

2.2. Scope

The reliability of waste-filled storage canisters was considered in relation to the reference design features of the storage facility and the properties of the waste and canister materials in terms of their complete life history of formation, packaging, handling, shipping, and storage--that is, all factors that have an influence on reliability. Container degradation due to internal metallurgical characteristics, thermal and mechanical events occurring during its life, and interactions of the canister material with internal and external environments were considered. Environments included operations in which the canisters are filled with high-level solid waste in its reference forms, interim storage at a reprocessing plant, transport from the reprocessing plant to a Retrievable Surface Storage Facility (RSSF), interim storage at the RSSF, and transport to the ultimate disposal site. The study was restricted to two generic waste forms, "calcine" and "glass" defined by the reference design. Waste solidification processes were not considered; the properties of calcine and glass were considered in terms of general chemical nature within the range of the reference system concepts. Limited consideration was given to systems design and to reliability methodology in determining overall reliability because of the limited performance data available for analysis. In order to estimate reliability, a broad review of relevant materials chemistry was made.

3. DESCRIPTION OF REFERENCE SYSTEMS

The reference systems used in this analysis were developed from several kinds of information. Three conceptual designs[1] of the RSSF, as presented in reference 1, were supplemented by information obtained during a visit with BNWL and ARHCO personnel. Where design or reference information on some portion of the system was not available, design criteria were used where possible to establish a reference. Where we lacked design criteria, we resorted to our own best judgment.

The principal chronological reference sequence has already been identified in Section 2. It is repeated here showing time intervals and some additional detail.

    a. Fabrication and testing of canisters
    b. Filling of canisters with the selected waste form at the reprocessing plant; cooling time of waste: 1 yr
    c. Closure of canisters
    d. Interim storage at the reprocessing plant for a period of 9 yr.
    e. Shipment in a water-cooled cask* to the RSSF after a cooling time of 10 yr
    f. Interim storage at RSSF for 100 yr by one of three methods:
        1. Water Basin Concept (WBC)
        2. Air-Cooled Vault Concept (ACVC)
        3. Sealed Storage Cask Concept (SSCC)
    g. Shipment to permanent disposal site

A second chronological reference sequence examined eliminates interim storage at the RSSF and extends interim storage at the reprocessing plant to forty years. Thus, steps e and f in the above list would be eliminated, and step d modified to reflect forty-year storage.

Each of these steps is treated in greater detail below.

3.1. Fabrication and Testing of Canisters

The reference material for the canister for this study[2] is stainless steel type 304L. This is consistent with the identification of "300 series stainless steel" in reference 2 and of "304L stainless steel" in a chapter of the same reference contributed by a metallurgical consultant.[3] Reference 1 does not state a rationale for alloy selection. Discussions with personnel from BNWL and ARHCO reveal that no definitive selection of an alloy has been made, but that for reference purposes, 304L is a representative alloy having generally good high-temperature properties and corrosion resistance and a well-developed fabrication technology. (As indicated in later sections, stainless steel 304 has properties similar to 304L, except the latter is less susceptible to sensitization.)

---

* Shipment in a water-cooled cask was assumed because of heat-transfer advantages of current technology for water-cooled shipments of spent fuel. Reference 1 of Section 3 does not identify shipments by type, but ARHCO personnel have indicated in private communications that the RSSF is not designed to accept water-filled casks.

Requirements for design and fabrication of the canister have been drawn principally from a draft version of canister acceptance criteria[*] developed by ARHCO.[4] The design material is 304L stainless steel, and the design temperature and pressure are 650°F (343°C) and 150 psig (1.03 MN/m^2). According to reference 4, design and fabrication shall be designated Class A quality level as defined in NRC Regulatory Guide 1.26, and the quality assurance program shall conform to the requirements of 10 CFR Part 50, Appendix B. The ASME Boiler and Pressure Vessel Code Section III (Division 1) shall be used as a guide for design, fabrication, and examination. Since all canisters will be exposed to a water environment at the reprocessing plant and perhaps during shipment (regardless of the storage mode at the RSSF), the reference condition adopted here is that all fabricated canisters will be subjected to full stress relief, and that closure welds (after filling with waste) will be subjected to local stress relief.

3.2. Filling Canisters with Waste

3.2.1. Calcine

The process of calcination can be performed in a variety of ways in different equipment types, including spray driers, pot calciners, fluidized-bed calciners, and rotary calciners. Typical operating temperatures are in the range of 450 to 550°C. To effect removal of various impurities or residual nitrates and water, the calcine may be given a post-treatment with or without vacuum at temperatures in excess of 800°C. Chemical post-treatments with hydrogen or other materials are also possibilities. A post-treatment at 800°C is the reference condition established for this report.

The reference filling condition adopted in this study assumes that calcine will be cooled to a temperature of 400°C or lower and that the maximum temperature of the canister during filling will also be 400°C. The preparation and loading of the calcine occurs at a cooling time of one year.

Reference compositions of high-level waste are given in Section 4.

---

[*] A more recent draft version of canister acceptance criteria[5] does not include most of the items in this paragraph, i.e., design material and pressure, design and fabrication as specified in Regulatory Guide 1.26, and the requirements of 10 CFR Part 50, Appendix B, and the ASME Boiler and Pressure Vessel Code Section III (Division 1). For purposes of this report, however, the items have been retained for the reference concept description. The new version addresses criteria for the Sealed Storage Cask Concept only. The shipper, in his design, must consider that "...the maximum normal operating temperature of the waste canister at the RSSF is 650°F." Further, "pressure effects, [regardless of source]...shall be based on the shipper's evaluation of the conditions during processing, storing, and shipping. The waste canister must provide adequate structural integrity in the wall and the closure to allow normal hot cell handling operations at the conclusion of a 100-year storage period. External corrosion...shall be assumed to be 10 mils for up to a 100-year storage time."

3.2.2. Glass

The reference sequence provides for preparation of the glass waste form in the canister itself; this is referred to as in-can melting. The reference glass has a borosilicate composition and is prepared at a cooling time of one year.

The canister is held in a furnace that is capable of zone heating; the hot zone follows the glass level upward as melting proceeds. Frit and calcine are added together at a ratio of three to one, with the temperature in the fusion zone held in the region of 950 to 1000°C. After a melt cycle of about 14 hr, the canister and its contents are cooled rapidly through the first 200°C at a rate of about 100°C/hr. Rapid initial cooling is required to minimize or avoid sensitization of the stainless steel canister in the critical region of 450 to 800°C. Subsequent cooling is conducted at a lower rate of about 25°C/hr. A separate furnace may be utilized for the slow cooling cycle to release the melting furnace for a new batch.[6]

Any gases evolved due to volatilization or reaction are vented from the canister.

3.3. Canister Closure

Closure of the canister is effected by welding a suitably designed cover into the top. Because the welding operation will result in the development of local high stress levels, the reference design provides for a local stress relief treatment in the temperature range of 850 to 900°C. This range is adopted to avoid temperatures in which sensitizing of the stainless steel can occur. It is realized that the welding operation itself introduces temperature gradients in the vicinity of the weld which will result in some sensitizing (which will not be removed by the stress relief treatment), but this is expected to be insignificant because of the short duration at such temperatures.

3.4. Interim Storage at the Reprocessing Plant

The filled and sealed canister will be stored under demineralized water for a reference period of nine years. The water conditioning system is capable of dissipating sufficient quantities of heat so that the temperature of the water will not normally exceed 128°F (53°C). The chloride ion concentration in the water will be kept below 10 ppm. Chloride concentration control is important in inhibiting the development of stress corrosion cracking in stainless steel canisters.

The technology of water demineralization is such that a chloride concentration level of 10 ppm should be easily achievable. Experience at several nuclear reactors has been described,[7] including experience with primary and secondary coolant loops of pressurized water reactors (PWRs), the single loop in boiling water reactors (BWRs), and fuel storage pools. In the primary loops of PWRs, side streams containing 0.3 to 0.6% chloride pass through mixed-bed ion-exchangers which are typically capable of maintaining chloride levels below 1 ppm. In secondary systems, chloride levels have been held below 0.3 ppm by a combination of five percent bypass flow through mixed bed demineralizers, controlled blowdown, and controlled in-leakage at the condenser.

In BWRs, full flow of the coolant through demineralizers lowers chloride levels to less than 0.1 ppm. In the fuel storage pool at Unit 1 of the Indian Point Nuclear Power Station, flow of 100 gpm through a demineralizer has been able to maintain chloride concentration at about 1 ppm.

Special resins have been developed for nuclear service that do not introduce undesirable impurities in the effluent streams.[7] Special attention has been given to reducing the concentrations of leachable impurities in the resins and to producing uniform bead size.

The ability of a water purification system to achieve specified chloride levels is also dependent on the design, materials of construction, and sources of contamination of a storage pool. It is assumed in this report that these factors are adequately controlled.

3.5. Shipment to the Retrievable Surface Storage Facility

The reference system provides for the shipment of waste canisters by rail in large casks, using water as a coolant. It provides that a cask meets all of the requirements of 10 CFR Part 71, including the series of tests of Appendix B of that part. The cask design includes a provision for heat dissipation that limits the temperature of the coolant under normal conditions to 128°F (53°C). The cask is not equipped with a water treatment system. However, the water charged to the cask as coolant is the same type of water as is in the storage pool at the reprocessing plant. The cask is designed in such a manner that in the event of failure of the circulating coolant system (*e.g.*, pump failure), the temperature of the coolant will rise to a maximum of that equivalent to a pressure of 500 psig (34 atm); that is, 243°C. Such a design is compatible with the current state-of-the-art technology.

Conceptual designs of casks for the shipment of high-level wastes have been developed by Oak Ridge National Laborator.[8,9] These casks utilize dry shipment and depend on the transfer of heat from the waste canisters to the inner cavity wall by radiation. Temperatures of the canister wall are thus considerably higher than those developed for the reference case. The effect of dry shipment on the canister is discussed as an alternative in Section 3.7.6.2.

3.6. Interim Storage at the RSSF

Three concepts of interim storage as described in reference 1 constitute alternative reference designs for this study: (1) the Water Basin Concept (WBC), (2) the Air-Cooled Vault Concept (ACVC), and (3) the Sealed Storage Cask Concept (SSCC).

3.6.1. Water Basin Concept

The waste canisters are stored in a water-filled pool that has a capacity of 500 canisters. Additional pools (modules) are put in service as required by the receipts. The water treatment system is capable of dissipating sufficient heat to maintain the pool water temperature (under normal conditions) at 128°F (53°C), and contains demineralization equipment that maintains the chloride ion concentration at 10 ppm or less. These capabilities are within the state-of-the-art technology.

3.6.2. Air-Cooled Vault Concept

In this reference concept, the storage unit is a waste-filled stainless steel canister sealed in a mild steel overpack and is stored and cooled in air moving by thermal convection. A sleeve surrounds the storage unit to enhance heat removal capability. Each storage vault (module) has a capacity of 500 storage units, and modules are added as required.

3.6.3. Sealed Storage Cask Concept

In this storage concept, canisters containing waste are sealed in an overpack of mild steel, placed inside (but not sealed) in a free-standing cylindrical concrete shield, and stored outdoors on a concrete pad. Cooling is effected by thermal convection of atmospheric air over the surface of the overpack by means of openings provided in the top and bottom of the outer concrete shield.

3.7. Reference Heat Loadings and Canister Dimensions

3.7.1. General

The unique characteristic of fission product wastes that must be accommodated is the self-generation of heat, which is very high when the fission products are generated and decreases significantly with time. The ability to remove the heat is dependent on geometric configurations, temperature of the heat sink, maximum allowable temperature of the waste, and the thermal conductivity of the waste. For a cylindrical form, the equation relating these factors is

$$T_c - T_s = \frac{q_o r^2}{4\ kf} \tag{1}$$

where

T_c = waste centerline temperature, °F

T_s = canister surface temperature, °F

q_o = waste heat rate, Btu/(hr)(ft^3)

r = canister radius, ft

k = thermal conductivity, Btu/(hr)(ft)(°F)

f = fin factor* (f=1 if no fins are used)

The reference waste described in Section 4 is produced from the processing of LWR fuels having a burnup of 33,000 MWd/MT.** For the purposes of this report, the approximate heating rate expressed as kilowatts per tonne, is taken as 11, divided by the cooling time in years. Deviations from actual heat rate data[10] are small for cooling times ranging from 1 to 100 yr, which is the time period relevant to the discussions and conclusions of this report.

---

* A discussion of the fin factor as used here is given in Section 8.3.2.

** MT = metric ton (tonne)

The reference procedure in waste management adopted for the purposes of this report specifies the preparation of solid waste forms and the filling of canisters after one year of cooling. Allowable canister sizes are determined by the maximum allowed centerline temperatures of the waste, the specified temperature of the water coolant, the heat rating of the waste (11 kW/MT), the thermal conductivity of the waste, and the fin factor (where applicable). The calculated canister diameters, of necessity, are small for these conditions. Had a reference procedure been adopted that considered the conversion of waste to solids at a later date, allowable canister sizes would have been larger. In those cases where calculated diameters (for one-year-cooled wastes) were less than 6 in. (15.2 cm), a six-inch canister was used and a cooling time (longer than one year) was determined to satisfy the other criteria.

3.7.2. Glass Waste Form

The following reference data for the glass waste form are taken from Section 4.2.2.:

Density: 3.5 g/cm^3
Volume: 2.6 ft^3/MT of fuel (0.0736 m^3/MT)
Thermal conductivity*: 0.6 Btu/(hr)(ft)(°F)[1.038 W/(m)(°C)]

At a cooling time of one year, the specific heat generation rate of the filled canister is equivalent to 11 kW for the fission products associated with one tonne of fuel. For the reference glass, this corresponds to 4.23 kW/ft^3 (149.4 kW/m^3). The reference maximum centerline temperature of waste in the glass form at one-year cooling is 1472°F (800°C),[11] and the canister wall temperature is that of the coolant in the storage pools, 128°F (53°C). Substitution of these values (and using f = 1 for the case of no fins) into equation 1 yields a canister diameter of 11.34 in. (28.8 cm).

3.7.3. Calcine Waste Form (with fins)

The following reference data for the calcine waste form are taken from Section 4.2.1.:

Density: 2.0 g/cm^3
Volume: 1.2 ft^3/MT of fuel (0.034 m^3/MT)
Thermal conductivity*: 0.2 Btu/(hr)(ft)(°F) [0.346 W/(m)(°C)][11,12]
Fin Factor**: 4

The incorporation of fins for the reference case increases the effective thermal conductivity of the calcine by a factor of four. The volumetric heat generation rate for the reference calcine at the time of filling (one-year cooling) is 9.17 kW/ft^3 (323.8 kW/m^3). The maximum centerline temperature of waste in the calcine form is 1112°F (600°C),[11] which is 360°F (200°C) less than that for glass. The canister wall temperature is again that of the coolant, 128°F (53°C). Substitution of these values into equation 1, yields a canister diameter of 7.61 in. (19.3 cm).

---

* For comparison, see Appendix A for calculational results based on a model that provides for variation of thermal conductivity with temperature.

** A fin factor of four is obtained by incorporating radial metallic fins occupying about five percent of the canister cross section. This is shown in Section 8.3.2.

Waste in the glass form in a 11.34-in. (28.8-cm) canister contains 2.4 percent more fission product oxides than does calcine waste in a 7.61-in. (19.3-cm) canister.

3.7.4. Calcine Waste Form (no fins) in Six-Inch (15.2-cm) Canisters (Alternative to the reference case)

For one-year cooling, equation 1 results in a canister diameter of less than 6 in. (15.2 cm) for calcine if no fins are to be used. A 6-in. (15.2-cm) canister is the smallest canister presently considered as acceptable for use in the RSSF. The heat rate that is compatible with a 6-in. (15.2-cm) canister is found, via equation 1, to be 3.69 kW/ft^3 (13.03 kW/m^3). A delay of 2.5 yr before preparation of the calcine would yield this heat rate.* Nearly twice as many canisters would be needed as for waste in the glass form under reference conditions.

3.7.5. Calcine Waste Form (no fins) in Canisters Having a Fission Product Capacity Equivalent to the Capacity of Canister Selected for Glass (Alternate to the reference case)

For calcine waste, a canister with a diameter of 7.71 in. (19.6-cm) would contain fission products equivalent to the quantity in glass in a 11.34-in. (28.8-cm) diameter canister. Thus the number of canisters required would be equivalent. The heat rate compatible with a 7.71-in. (19.6-cm) canister is 2.24 kW/ft^3 (79.1 kW/m^3). For this case, a cooling time of 4.1 yr is indicated before the calcine would be prepared.*

3.7.6. Reference Shipment Temperatures

3.7.6.1. Water Cooling**.

The reference shipment for solidified wastes provides for cooling with water, controlled under normal conditions at 128°F (53°C). At the time a canister is filled with glass (cooling time of waste: 1 yr), the heat rate is 4.23 kW/ft^3 (149.4 kW/m^3). The initial canister wall temperature during storage at the reprocessing plant would be 128°F (53°C), and the centerline temperature of the glass would be 1472°F (800°C), which is the reference design maximum. At the time of shipment (cooling time: 10 yr), the heating rate and the temperature differential across the waste form are each reduced by a factor of ten. The temperature differential is then 134°F (56°C) and the glass centerline temperature is 262°F (128°C). These modest heat-removal requirements can be readily accommodated when waste is shipped in the glass form.*

Similar analyses have been made for the reference calcine waste (canister equipped with internal fins), as well as for two other calcine cases (canister contains no fins) described in Sections 3.7.4.

---

* For comparison, see Appendix A for calculational results based on a model that provides for variation of thermal conductivity with temperature.

** Shipment in a water-cooled cask was assumed because of heat-transfer advantages of current technology for water-cooled shipments of spent fuel. Reference 1 of Section 3 does not identify shipments by type, but ARHCO personnel have indicated in private communications that the RSSF is not designed to accept water-filled casks.

and 3.7.5. The results of these analyses are shown in Table 3.1. In all cases, centerline temperatures of the wastes are below reference maxima.

Because the conditions of shipment in a water-cooled cask are identical to underwater storage at the processing plant, shipment could be made at a cooling time of 10 yr for all cases described here.

3.7.6.2. Air Cooling

An analysis has been made of the shipment of high-level wastes in a dry condition. The basis for the analysis is a study made at Oak Ridge National Laboratory for casks weighing 100 tonnes.[8] These casks are designed for the shipment in each cask of thirty-six 6-in. (15.2-cm) canisters or nine 12-in. (30.5-cm) canisters. Heat dissipation from the canisters to the cask was assumed to occur principally by radiation. Figure 3.1 shows canister wall temperatures of the centermost canister in the shipment configuration as a function of waste heat rate for several canister diameters. This information was used to determine waste centerline temperatures and canister wall temperatures for our cases at the time of shipment.

Lines (a) through (d), superimposed on Fig. 3.1, show the relationship of canister wall temperature to thermal power, using equation 1. The slope of each line is $r^2/4kf$. The lines correspond to four waste cases described in Sections 3.7.2 through 3.7.5.

Case (a) Glass waste form prepared in 11.34-in. (28.8-cm) canister after 1-yr cooling

Case (b) Calcine waste form (with fins) prepared in 7.61-in. (19.3-cm) canister after 1-yr cooling

Case (c) Calcine waste form (no fins) prepared in 6.0-in. (15.2-cm) canister after 2.5 yr cooling

Case (d) Calcine waste form (no fins) prepared in 7.71-in. (19.6-cm) canister after 4.1-yr cooling

Line (a) was positioned to pass through point 1, which is the thermal power (after 10-yr cooling) of the 11.34-in. (28.8-cm) caniter. Point 1 corresponds to a canister wall temperature of 716°F (380°C). The intersection of line (a) with the ordinate yields the glass centerline temperature of 850°F (454°C), which is within the specified maximum of 1472°F (800°C).

Line (b) was positioned to pass through point 2, which is the thermal power (after 10-yr cooling) for the 7.61-in. (19.3-cm) canister (equipped with fins) for the calcine form. Point 2 corresponds to a canister wall temperature of 1014°F (546°C). The intersection of line (b) with the ordinate yields the centerline temperature of 1112° (600°C), which is the maximum allowable temperature for the calcine.

For 10-year cooling, lines (c) and (d) would also pass through point 2. However, the slopes of the lines are such that the lines would intersect with the ordinate at centerline temperatures well in excess of the allowable 1112°F (600°C). Hence, lines (c) and (d) were constructed (with appropriate slopes) to intersect the ordinate at 1112°F (600°C), the maximum centerline temperature. The intersections with the appropriate

TABLE 3.1. Conditions of Shipment of Waste Forms with
Water Cooling at a Cooling Time of Ten Years[a]

| Waste Form | Cooling Time at Filling (yr) | Waste Form Diameter, in.(cm) | Heat Rate(kW/ft^3)[b] | | Shipping Temperatures, °F(°C) | |
			At Filling	At Shipment	ΔT across Waste Form	Waste Centerline
Glass	1	11.34 (28.8)	4.23	0.423	134 (74)	262 (128)
Calcine						
with fins	1	7.61 (19.3)	9.17	0.917	98 (54)	226 (108)
with no fins	2.5[c]	6.0 (15.2)	3.69	0.917	246 (137)	374 (190)
with no fins	4.1[d]	7.71 (19.6)	2.24	0.917	403 (224)	531 (277)

[a] See footnotes on page 12.

[b] To convert to kW/m^3, multiply by 35.3.

[c] Cooling time required to permit the use of 6-inch canisters.

[d] Cooling time required to allow use of canister having waste capacity equivalent to that for glass.
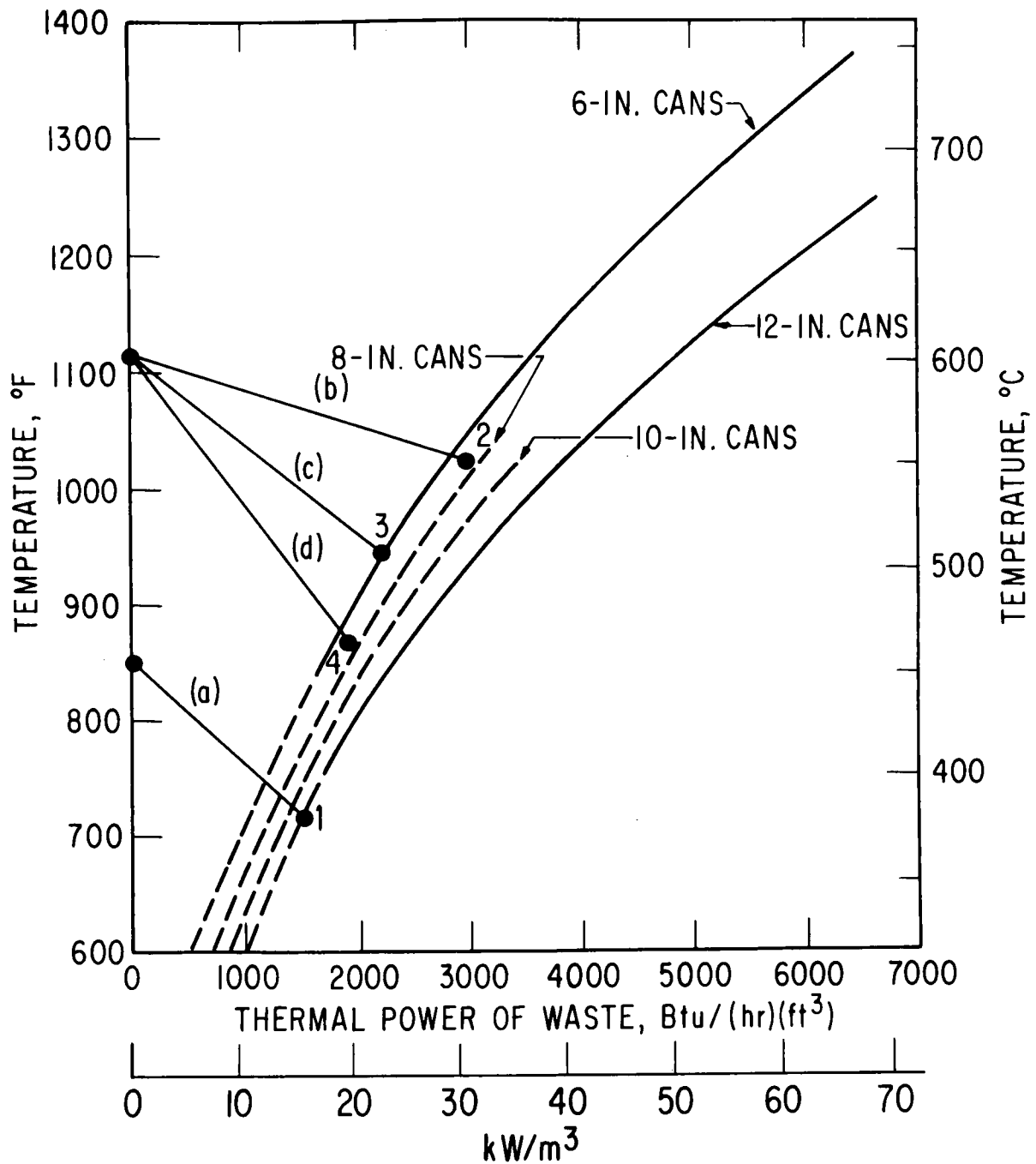
Fig. 3.1. Surface Temperature of the Hottest Canister in a ∿100-Ton Dry Cask.[8]
(Dashed lines added for this report)

Terminal points of lines (a) through (d) show waste centerline temperatures
and canister wall temperatures.

(a) Glass in 11.34-in canisters shipped after 10-yr cooling
(b) Calcine (with fins) shipped in 7.61-in. canisters after 10-yr cooling
(c) Calcine (no fins) shipped in 6-in. canisters after 14.2-yr cooling
(d) Calcine (no fins) shipped in 7.71-in. canisters after 16.0-yr cooling

canister diameters (points 3 and 4) lead to canister wall temperatures, waste thermal powers, and cooling times for shipment that meet requirements. For case (c), a cooling time of 14.2 years is required, and the canister wall temperature will be 940°F (504°C). For case (d), the corresponding values are 16.0 years and 865°F (463°C). The results are summarized in Table 3.2.

In all three calcine cases [(b) through (d)], the canister wall temperatures during air-cooled shipments for the centermost canisters are sufficiently high to risk considerable sensitization of the reference type 304L stainless steel. This may well be acceptable if subsequent storage at the RSSF is under air-cooled conditions, but is probably unacceptable if water-cooled storage at the RSSF is to be used.

TABLE 3.2. Conditions of Shipment of Waste Forms in a Dry Cask

Waste Form	Cooling Time at Filling (yr)	Cooling Time at Shipment (yr)	Heat Rate(kW/ft^3)[a]		Shipping Temperatures, °F(°C)		
			At Filling	At Shipment	Waste Centerline	Canister Wall	ΔT
Glass							
11.34 in.	1	10	4.23	0.423	850 (454)	716 (380)	134 (74)
Calcine							
7.61 in. with fins	1	10	9.17	0.917	1112 (600)	1014 (546)	98 (54)
6.00 in. with no fins	2.5[b]	14.2	3.69	0.645	1112 (600)	940 (504)	172 (96)
7.71 in. with no fins	4.1[c]	16.0	2.24	0.571	1112 (600)	865 (463)	247(137)

[a] To convert to kW/m^3, multiply by 35.3.

[b] Cooling time required to permit the use of 6-in. canisters.

[c] Cooling time required to allow use of canister having waste capacity equivalent to that for glass.

References for Section 3

1. Retrievable Surface Storage Facility. Alternative Concepts Engineering Studies, AEC Report ARH-2888 Rev. (July 1974).

2. ibid., pp. 5-35.

3. ibid., pp. 11-13.

4. D. E. Larson and R. J. Thompson, Retrievable Surface Storage Facility Acceptance Criteria for Canister and Shipping Cask, Draft, ARCHO, (Jan. 17, 1975).

5. "Acceptance Criteria for the Waste Canister and Shipping Cask for the Retrievable Surface Storage Facility," draft (April 30, 1975), courtesy of D. C. Nelson, ARHCO.

6. R. Kennedy, ARHCO, personal communication (January 1975).
   Also, Quarterly Progress Reports, Research and Development Activities, Waste Fixation Program, J. L. McElroy (comp.):
   July through September 1974, pp. 12-13, BNWL-1871
   October through December 1974, pp. 5-11, BNWL-1893
   January through March 1975, pp. 12-14, BNWL-1908
   April through June 1975, pp. 5-9, BNWL-1932

7. S. B. Applebaum, Demineralization by Ion Exchange, Ch. 11, Demineralizing Water Treatment in Nuclear Power Plants, Academic Press, New York (1968).

8. J. J. Perona, R. S. Dillon, and J. O. Blomeke, Design and Safety Considerations of Shipping Solidified High-Level Radioactive Wastes, ORNL-TM-2971 (December 1970).

9. J. M. Holmes, Cask and Waste Container Cooling Studies, ORNL-TM-3545 (September 1971).

10. Siting of Fuel Reprocessing Plants and Waste Management Facilities, compiled and edited by the Staff of the Oak Ridge National Laboratory, ORNL-4451 (July 1970).

11. W. K. Eister, ERDA, personal communication.

12. Reference 1, pp. 6-26.

4. MATERIAL-CHEMISTRY CHARACTERISTICS OF REFERENCE FORMS OF SOLID WASTE

4.1. Introduction

The reference concept of canister storage of high-level radioactive waste includes two solid waste forms, calcine and glass. In Section 4, the waste forms are discussed as the first stage of the overall waste-canister-environment system for long-term retrievable storage. The reference concept defines the waste forms in broad terms of the waste origin and the waste-treatment operations: (1) evaporation-calcination and (2) vitrification (glass-making). The present discussion reviews the range of chemical and solid-state properties of these waste types in order to define their potentialities for stability, inertness, and compatibility with the canister and the other elements of the waste-storage system. Prevention of deleterious effects to the canister is the chief purpose of (a) specifications limiting heat generation rate in the waste, and (b) temperature-control requirements which are imposed throughout the waste handling and storage operations.

The most important properties of the solid waste forms relevant to canister containment are (1) those which are affected by temperature levels, temperature gradients, and temperature changes and (2) those which have the potential for pressurizing the canister or subjecting it to corrosion by liquified (molten) waste. Chemical properties determining these effects include free energies of oxide compounds, solid-liquid equilibria, plastic and viscous behavior, crystallization and crystal growth rates, solid diffusion and segregation phenomena, energy of internal surfaces (pores), vapor pressure of specific species, density, and thermal conductivity. To describe these properties of the waste forms adequately, the discussion employs a general chemical terminology based primarily on two sources: (a) a comprehensive scientific survey of ceramics[1] and (b) a summary of basic and commercial glass technology.[2]

The important waste properties are themselves resultants of the nature of fission product elements and the particular conditions used in solidification (calcination or vitrification). The present state of knowledge of these chemical properties is not adequate to establish directly the basis for establishing the controls necessary to assure reliability.

4.2. Properties of Calcine and Glass

4.2.1. Reference Calcine

The chemical constitution of the calcine is determined by (a) the spectrum of fission-product elements produced in the fission process, (b) the temperature, oxidation potential, physical agitation, and the extent of removal of gaseous, volatile, and decomposable constituents in the evaporation and calcination steps, and (c) the addition of non-fission product elements in processing steps.

Table 4.1 shows the reference compositions of the high-level liquid waste generated at the spent-fuel reprocessing plant and of

TABLE 4.1. Reference Compositions of High-Level
Liquid Waste and Calcined Oxide[3]

	Constituent	Concentration, in Liquid Waste, mol/liter at 378 liters/MTU	Oxide	kg oxide/MTU
Inerts	HNO_3	2.0		
	Na	0.01	Na_2O	0.117
	Fe	0.10	Fe_2O_3	3.022
	Cr	0.012	Cr_2O_3	0.345
	Ni	0.005	NiO	0.141
	PO_4	0.10	P_2O_5	2.686
	Gd	0.151	Gd_2O_3	10.360
				16.671
Fission Products	Rb	0.010	Rb_2O	0.354
	Sr	0.027	SrO	1.059
	Y	0.014	Y_2O_3	0.598
	Zr	0.016	ZrO_2	4.944
	Mo	0.095	MoO_3	5.176
	Tc	0.022	Tc_2O_7	1.291
	Ru	0.059	RuO_2	2.972
	Rh	0.010	Rh_2O_3	0.480
	Pd	0.032	PdO	1.483
	Ag	0.002	Ag_2O	0.088
	Cd	0.002	CdO	0.097
	Te	0.012	TeO_2	0.725
	Cs	0.054	Cs_2O	2.880
	Ba	0.027	BaO	1.567
	La	0.024	La_2O_3	1.480
	Ce	0.051	CeO_2	3.323
	Pr	0.023	Pr_6O_{11}	1.482
	Nd	0.071	Nd_2O_3	4.522
	Pm	0.0019	Pm_2O_3	0.123
	Sm	0.014	Sm_2O_3	0.924
	Eu	0.003	Eu_2O_3	0.200
	Gd	0.002	Gd_2O_3	0.137
				35.905
Actinides	U	0.110	U_3O_8	11.689
	Np	0.0085	NpO_2	0.865
	Pu	0.001	PuO_2	0.103
	Am	0.0018	Am_2O_3	0.181
	Cm	0.004	Cm_2O_3	0.040
				12.878
	Total			65.5

the calcine resulting from solidification processing.[3] The waste is typical of that produced from the processing of LWR fuels having a burnup level of about 33,000 MWd/MT, using a Purex-type flowsheet that utilizes gadolinium as a means of criticality control. The bulk density of the calcined oxide is two,* and the calcine occupies a volume of 1.2 cu ft for each tonne of fuel processed.

The heating rate of the oxides varies nearly inversely with the cooling time between 1 and 100 years cooling. For purposes of this report, the heating rate of the fission products (expressed as kilowatts per tonne of fuel) is taken as 11 divided by the cooling time in years. Deviations from more exact heat-rate data[4] are small and negligible for the time period of interest in the discussions and conclusions of this report.

The thermal conductivity of the calcine is taken to be 0.2 Btu/(hr)(ft)(°F) [0.35 W/m°C].*

Because the fission products in the waste generate heat by radioactive decay, a major requirement of storage is temperature control by the removal of heat. Residual nitrate and water in the calcine are subject to both thermal and radiolytic decomposition into gaseous products, so that a confined volume of calcine will be filled with these decomposition products. (The quantities of residual nitrates and water depend on prior treatment. The reference composition is 0.1 wt % of each). The pressure exerted by these gases depends on the amount of residual nitrate and water, the extent of decomposition, and the temperature and volume of the containment space.

4.2.2. Reference Glass

The reference glass is a borosilicate glass that can be prepared at temperatures of 950 to 1000°C. Glass-making additives are combined with calcine oxides in the ratio of about three to one, which results in a glass having a reference density of 3.5 g/cm^3. The volume of glass required to contain the calcined oxides from one tonne of fuel is 2.6 ft^3. The thermal conductivity is taken to be 0.6 Btu/(hr)(ft)(°F).

4.3. Properties of Fission Product Oxides

In this section, the chemical nature of individual oxide compounds is discussed; in section 4.5 below, some discussion of the solid state mixed-oxide matrix is presented.

Of the total fission product element mass of 35.1 kg/tonne fuel, fission products in the calcine weigh 28.4 kg/tonne (see Table 4.2). Thus, 17.6 wt% of the total fission products are lost as gases (Xe, Kr, I, Br, etc.) in the processing steps prior to calcination. In Table 4.2, the composition of the residual calcine is given for the elements in weight percent. Also included is information on melting points, volatility, and free energies of formation at 1000°C. These properties are relevant to the stability and inertness of the solid waste.

---

* The bulk density and thermal conductivity are low because the solid is poorly consolidated, friable, and porous, with about a 65% void fraction.

TABLE 4.2. Oxides in High-Level Waste Calcine

	Fission Product		Waste Solution		Oxide Calcine[a]			
FP element	g Element[4] kg Fuel(U)	wt % of Elements in Calcine	Oxide[3]	g Oxide[3] kg Fuel(U)	Oxide in Calcine (wt%)	Oxide[5] Melting Point (°C)	Oxide[6] ΔG_f°(1000°C) (kcal/g-atom oxygen)	Comments[6] on Oxide
Nd	4.15	14.6	Nd_2O_3	4.52	12.8	∿1900	−116	
Zr	3.77	13.3	ZrO_2	4.94	14.0	2750	−103	
Mo	3.47	12.2	MoO_3	5.18	14.6	795 (MoO_2)	−36	
Ce	2.64	9.30	CeO_2	3.32	9.38	1692 (Ce_2O_3)	−103	
Cs	2.32	8.17	Cs_2O	2.88	8.13	762	−20	decomp 460°C
Ru	2.14	7.54	RuO_2	2.97	8.39	1130	∿0	decomp 1000°C
Ba	1.79	6.32	BaO	1.57	4.42	1923	−105	
Pd	1.41	5.96	PdO	1.48	4.19	870	>0	
La	1.27	4.47	La_2O_3	1.48	4.18	2315	−116	
Pr	1.20	4.22	Pr_6O_{11}	1.48	4.18	∿2000 (Pr_2O_3)	−116	
Sm	0.904	3.18	Sm_2O_3	0.924	2.61	2300	−116	
Tc	0.835	2.94	Tc_2O_7	1.29	3.64	--	−25 (TcO_2)	subl 1000°C
Sr	0.778	2.74	SrO	1.06	2.99	2430	−110	
Te	0.572	2.01	TeO_2	0.725	2.05	733	−10	volat ∿800°C
Y	0.465	1.63	Y_2O_3	0.598	1.69	2417	−113	
Rh	0.392	1.38	Rh_2O_3	0.48	1.33	1100	>0	decomp 1100°C
Rb	0.346	1.22	Rb_2O	0.354	1.00	∿500	−26	decomp 477°C
Eu	0.164	0.58	Eu_2O_3	0.200	0.56	2050	−113	
Gd	0.123	0.43	Gd_2O_3	0.137	0.39	2330	−113	
Pm	0.085	0.30	Pm_2O_3	0.123	0.35	∿2000	−116	
Cd	0.084	0.29	CdO	0.097	0.27	830	−26	decomp 900°C
Ag	0.060	0.21	Ag_2O	0.088	0.25	∿200	>0	decomp 300°C
Se	0.052	0.18	SeO_2			340	−10	
Sn	0.052	0.18	SnO			1080	−38	decomp 1080°C
Sb	0.011	0.04	Sb_2O_3			656	−30	subl 1500°C
Dy	0.001		Dy_2O_3			∿2000	−110	
Ho	0.00008		Ho_2O_3			∿2000	−110	
Er	0.00003		Er_2O_3			∿2000	−110	

Mass Total 28.4 g/kg fuel (U)
(kg/tonne)

Mass Total 35.9 g/kg fuel (U)
(kg/tonne)

[a] Oxide formulas given for calcine in parentheses were different from oxide formulas for waste solution (Column 4).

The fission product elements whose oxides are least stable are summarized in Table 4.3. Since some of these elements do not form oxides at about 1000°C, their overall stability in a solid matrix depends on the properties of the elemental form. The melting points and the boiling points of the elements are given in the table.

TABLE 4.3. Properties of Selected Elements[a] as Metals

Element	Wt % of Total	Melting Point (°C)	Boiling Point (°C)	$\Delta G°$, Formation of Oxide at 1000°C (kcal/g-atom oxygen)	
Mo	12.2	2620	3700	-36	
Cs	8.17	28	620	-20	
Ru	7.54	2430	3700	0	oxide decomposes
Pd	5.96	1555	2200	>0	oxide decomposes
Tc	2.94	2200	~4700	-25	
Te	2.01	452	1390	-10	
Rh	1.38	1955	>2500	>0	oxide decomposes
Rb	1.22	38	700	-26	
Cd	0.29	321	767	-26	
Ag	0.21	960	1950	>0	oxide decomposes
Se	0.18	220	688	-10	
Sn	0.18	232	2260	-38	
Sb	0.04	630	1380	-30	

[a] These elements are the fission products whose oxides are least stable and are most subject to decomposition at 1000°C. Taken from Table 4.2.

The rare earth elements, the elements La and Y, the alkali-earth elements, and Zr form stable oxides of high melting points and low volatility; these elements constitute about 61% of the total mass. The oxides of the noble metals, Rh, Pd, and Ag decompose at temperatures approaching 1000°C, but the elemental forms are high melting and have low volatility; these elements constitute 7.55% of the total. Ruthenium (7.5%) and technetium (3%) are noble metals whose oxides are fairly stable, but at sufficiently high oxygen potential they form higher oxides that are volatile. Molybdenum (12.2%) is a noble metal with a fairly stable, nonvolatile oxide. The alkali metals, Cs and Rb (9.4%), have oxides of only moderate stability at temperatures approaching 1000°C; their oxides and elemental forms are significantly volatile at about 600°C. The remaining elements (Te, Cd, Se, Sn, Sb), which constitute about 2.6% of the total, have fairly stable oxides.

Mobility under temperature gradients has been observed for oxides of Cs, Rb, and Ru at temperatures of about 600°C, and this would be expected from the above properties. The stabilization of these oxides at high temperatures depends on the oxide matrix, *i.e.*, on the formation of stable complexes and the oxygen potential. The chemical basis of stability of fission product oxides in calcine and glass is discussed further below.

Cesium and rubidium form complex oxide compounds with other metals having valences of 4 to 6. For example, Rb_2MoO_4 has a melting point of 929°C

and Cs_2MoO_4 has a melting point of 925°C. The oxides that form compounds with Rb_2O and Cs_2O include MoO_3, SiO_2, TiO_2, and Nb_2O_5.[7] The phase diagram of the Cs_2MoO_4-MoO_3 binary system shows a low-melting eutectic at 460°C.[8] The other oxide compounds also form eutectics. The melting and sintering behavior of fission product oxides is discussed below in Section 4.5.3.

Other oxides, for example, TeO_2, are known to form low-melting mixtures with oxides of pentavalent and hexavalent metals. TeO_2 is also volatile at 790-940°C. Volatility of either metal or oxide may lead to mobility, concentration and possible corrosion of steel; this is discussed in Section 6.

The vaporization of cesium molybdate, Cs_2MoO_4, has been measured in Knudsen effusion experiments in the range of 890 to 920°C in continuing studies on the oxygen potential and diffusion effects in oxide reactor-fuel materials.[9] The derived equation for the vapor pressure of solid cesium molybdate was found to be

$$\ln p \ (Cs_2MoO_4, \ atm) = (15.14 \pm 0.05) - (3.22 \pm 0.14) \times 10^4/T(°K)$$

where the vapor pressure has a precision of about ±5%. In related work, it was determined that only Cs_2MoO_4 molecules are vaporized from solid cesium molybdate and that the vapor phase consists of Cs_2MoO_4. The calculated partial pressures of Cs_2MoO_4 from the above equation for temperatures of interest are as follows:

Temperature (°C)	Pressure (atm)
600	3.6×10^{-10}
800	3.5×10^{-7}
1000	3.9×10^{-5}

These results are pertinent to the possible interaction of calcine or glass with the canister, as discussed later in Section 6.

The ideal of a stable and inert form for fission product waste is a solid of low vapor pressure and high melting point under storage conditions. While most of the fission product oxides in Table 4.2 have high melting points and low volatility, the practical concern that some components may form vapor or liquid phases capable of attacking the canister is the basis for the following discussion of chemical characteristics of the oxide mixtures that constitute the reference solid waste.

4.4. Decomposition of Residual Nitrate and Water in Fission Product Oxide Calcine

4.4.1. Introduction

The fission product oxides in calcine are prepared from an aqueous solution of nitrates in nitric acid. In this preparation, which is a rapid evaporation of water and nitric acid during calcination, the fission products first appear as a mixture of solid nitrates with some bound water.

Substantial dewatering and decomposition of the solid fission product nitrates occurs during calcination to form oxides; the higher the calcination temperature, the lower the residual nitrate and water content of the calcine product. For calcination temperatures below 400°C, these residual impurities in the fission product oxide calcine may be of the order of 1 wt %. The reference specification adopted above (in Section 4.2) for nitrate and water is 0.1 wt % for each. This lower specified value of residual impurities is based on the need to avoid high pressures inside the canister, resulting from the formulation of gaseous products of decomposition of residual nitrates and bound water; this low value is achieved by a post-calcination treatment at higher temperature.

4.4.2. Calculation of Chemical Decomposition

The chemistry involved in dewatering and denitration is illustrated by the standard heats of formation and free energies of formation of the barium compounds.[5] The standard state is 1 atm and 25°C.

Compound	ΔH°_f (kcal/g-mol)	ΔG°_f (kcal/g-mol)
$Ba(NO_3)_2 \cdot H_2O$	-254.5	-
$Ba(NO_3)_2$	-237.06	-190.0
$Ba(NO_2)_2$	-174.0	-
BaO	-133.5	-126.3

The dewatering reaction is

$$Ba(NO_3)_2 \cdot H_2O(solid) \rightarrow Ba(NO_3)_2(solid) + H_2O(gas)$$
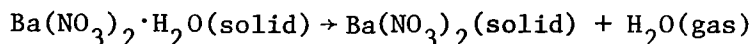
One mole of gas is produced for each mole decomposed. The reaction is endothermic, with a positive standard free energy of formation. The denitration reaction for complete decomposition (maximum gas production) is

$$Ba(NO_3)_2(solid) \rightarrow BaO(solid) + N_2(gas) + 5/2\ O_2(gas).$$
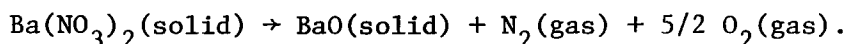
For each mole decomposed, 7/2 moles of gas are formed. The reaction is endothermic. Other reactions producing less gas can be postulated.

It should be noted that decomposition may also occur by radiolysis or by treatment with a chemical reductant.

The potential pressure from the decomposition of residual nitrate and water in a canister in which calcine is confined can be calculated for the system variables, assuming complete decomposition as well as ideal gas behavior in the void space of the bulk calcine. The following quantities are defined:

V is the total canister volume, cm^3
y is the void volume, when the canister is filled with calcine, as a fraction of V
x is the weight fraction of nitrate in the solid calcine

z is the weight fraction of water in the calcine

ρ is the theoretical density of calcine, g cm^{-3}

n_N is the moles of gas produced from complete nitrate decomposition

n_H is the moles of gas produced from complete decomposition of bound water

P is the pressure of gas in the void volume, atm

T is the temperature of the gas, °K

Then

$$n_N = V\rho(1 - y)(x)\frac{7/4}{62}$$

$$= 0.02823\ (x)(1 - y)V\rho$$

$$n_H = V\rho(1 - y)\frac{z}{18}$$

$$P = \frac{n_N RT}{Vy} + \frac{n_H RT}{Vy}\ ,$$

where the total pressure is the sum of terms for the pressure contributions of denitration and dewatering, respectively. For the gas constant R = 82.06 (atm)(cm^3)(g-mol)$^{-1}$(°K)$^{-1}$ and for ρ = 4.0 g/cm^3,

$$P(atm) = 9.26T\left(\frac{1 - y}{y}\right)(x) + 18.23T\left(\frac{1 - y}{y}\right)(z)$$

Note that the term for volume, V, has cancelled out and that the pressure ("the maximum pressure" for complete decomposition) is a function of the fraction of water and nitrate and of the temperature of the void space. For equal weights of nitrate and water (x = z), the pressure contribution of water is about twice that of nitrate. The pressure is also directly proportional to the factor $\rho(1 - y)$, which is the overall average density of waste in the canister, including the effects of the compound density, the void fraction, and "freeboard" in the canister.

In previous studies[10] related to the feed materials program-- single-stage fluid-bed evaporation, calcination, and denitration of uranyl nitrate solutions--the residual nitrate and water in uranium oxide product calcine was measured as a function of calcination temperature in the range 300 to 450°C. These results are presented in Fig. 4.1. At the same temperatures, the residual water contents were about one-fifth those of the residual nitrate, and the minimum residual nitrate was about 0.4 wt % at 450°C.[10] An extrapolation of the nitrate line indicates that a bed temperature of at least 800°C (1470°F) would be required to reduce the nitrate concentration to 0.1%. In the production of UO_2, treatment of the calcine with H_2 at 1100°C (2010°F) effectively eliminates nitrate and water by the joint effects of temperature and chemical reduction.
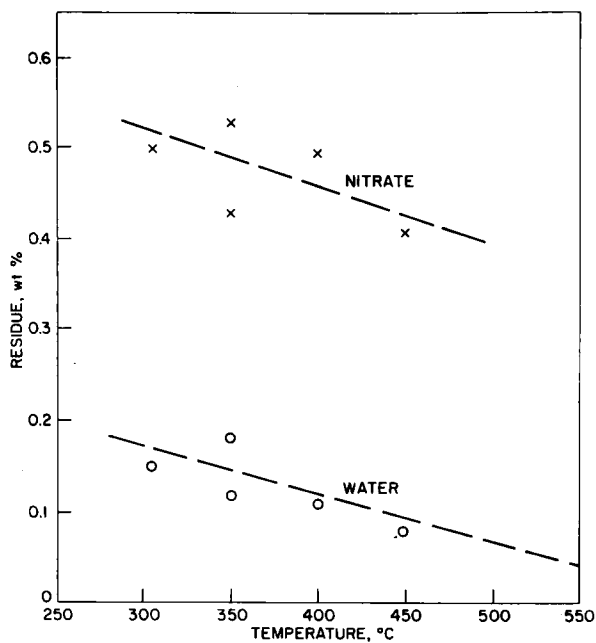
Fig. 4.1. Effect of Fluid-Bed Temperature on the Residual Nitrate and Water Content of the Product of Fluid-Bed Denitration of Uranyl Nitrate Solutions.[10]

The mathematical model for the decomposition pressure of residual nitrate in calcine, as derived above,

$$P(atm) = 9.26T \left(\frac{1-y}{y}\right)x,$$

is plotted in Fig. 4.2 for a temperature of 825°C as a function of the weight fraction nitrate in calcine (x) for three parameters of void fraction (y).
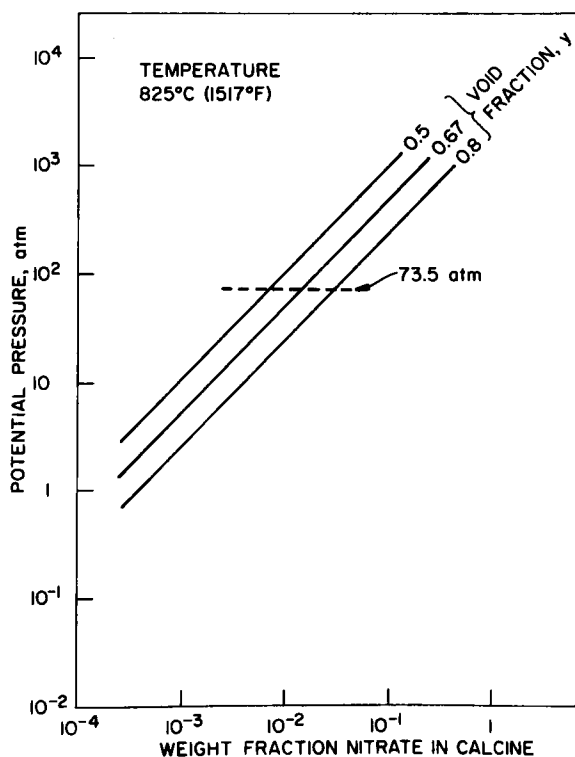
Fig. 4.2. Pressure at 825°C (1515°F) from Complete Decomposition of Residual Nitrate in Calcine.

This temperature was chosen as a high value of interest and in the range of small-scale tests of decomposition of synthetic calcines made at PNL.

The PNL decomposition data indicated that nitrate was fairly stable below 700°C (1290°F). The canister loading of 1.2 g cm^{-3} corresponded to a void fraction of approximately 0.70. The pressure observed corresponded to the complete decomposition of the nitrate present (about 2 wt %). In these tests, a pressurization of 1080 psi (73.5 atm) at 800°C (1470°F) was measured for a type PW-4b calcine.[11] This measurement is indicated as a horizontal dashed line on Fig. 4.2 to show the consistency of these results with the model.

These considerations show the chemical basis of the behavior of residual nitrate and water, and of the role of temperature on the pressure in a waste canister. Residual water and nitrate may have other effects also, such as corrosion. These other aspects of material chemistry and the specific effects of waste properties on canister integrity are described in later sections of this report.

4.5. Melting and Sintering of Fission Product Oxide Mixtures

4.5.1. Introduction

The melting behavior of mixed oxides can be related to the melting point of the pure oxides in terms of the solid structure, depending on whether a single solid phase is formed (a solid solution) or whether more than one solid phase is in equilibrium with the liquid (melting-point lowering by eutectic formation). These two types of equilibrium are exhibited for representative binary systems in Fig. 4.3.

The random substitution of one species of atom for another that takes place in the atomic lattice of a solid solution reaches an extreme in the case of the glass state, which is a single noncrystalline solid phase with no definite melting point.

The nature of calcine can be considered in relation to an ideal calcination process in which the original aqueous solution of fission products is dewatered and denitrated (at typical calcination temperatures) to a solid oxide mixture homogeneous on the atomic scale. The solid is not consolidated and has a high void fraction and internal surface. As the temperature of such a solid is raised, it undergoes densification, along with reduction of void fraction and internal surface. This phenomenon is sintering and is considered in Section 4.5.3. Here we are concerned with the temperature of melting, *i.e.*, the first appearance of a liquid phase as the temperature is increased.

Melting points of mixtures of materials may vary above and below the melting points of the individual components depending on the phase relationships of the constituents. The melting points of the pure oxides of fission product elements were given in Table 4.2. Modifications of melting points by other constituents can occur via the formation of solid solutions, eutectics, or compounds. Figure 4.3 illustrates the modification of the melting points of NiO and MgO by solid solution--that of NiO is raised and that of MgO is lowered. Eutectic formation, also illustrated in Figure 4.3, lowers the melting point below that of either constituent. The formation of compounds may result in melting points that exceed, are lower than, or intermediate to, the melting points of the constituent pure oxides. Consideration of additional components to form ternary, quarternary (and higher) systems
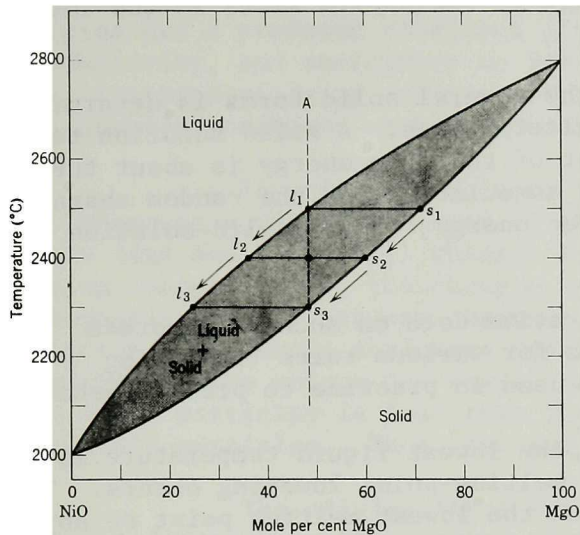
The binary system MgO-NiO.[1]
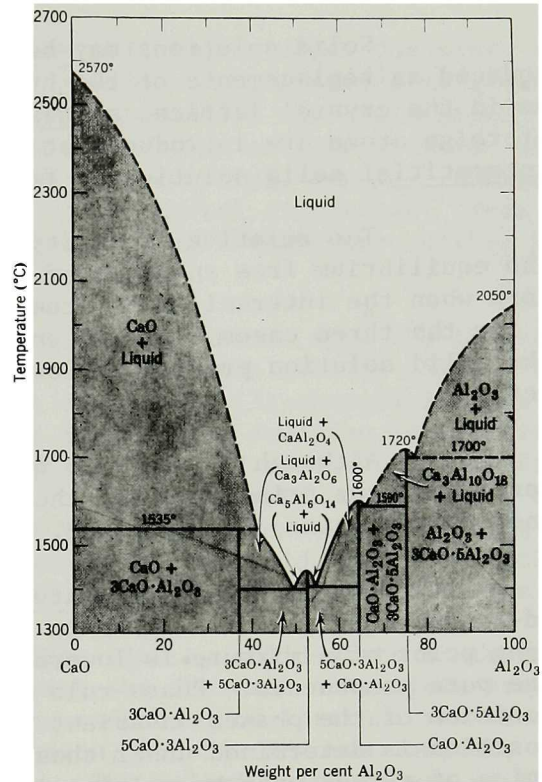
The binary system CaO-Al$_2$O$_3$.[1]

Fig. 4.3.   Illustration of Solid-Solution and Eutectic Phase Diagrams

constitutes another level of complexity. Thus, to predict the melting points of a mixture as represented by fission product oxides, and to estimate quantitatively the formation of liquid phase present as a function of temperature becomes exceedingly difficult, if not impossible. However, practical effects depend on the degree of homogeneity and on local melting in relation to canister reliability. The chemical basis of liquid phase formation is discussed in Section 4.5.2.

The melting behavior of crystalline material described above does not apply to glass formed from calcine. A characteristic of the formation of glass from the liquid state is that the composition and high rate of cooling do not allow crystallization to take place. Thus, the viscosity of liquid glass increases to the point of solid rigidity without having a definite melting point. Glass is discussed in Section 4.6.

4.5.2.   Compounds, Eutectics, and Solid Solutions[1]

A pure crystalline solid consisting of one kind of molecules can be modified to accommodate the introduction of a second kind of molecules by the formation of a compound, a eutectic, or a solid solution. In the formation of a compound, a new single crystal forms that incorporates the second kind of molecules with the first in an ordered manner. In formation of a eutectic, a second crystalline phase forms that incorporates only the second kind of molecules, thus yielding a mixture of two kinds of crystals, side by side. In the formation of a solid solution, the second kind of molecules is incorporated into the original single crystalline phase in a random manner.

Solid solutions may be of two types. If the foreign atoms are introduced as replacements of the host atoms at previously established locations in the crystal lattice, a substitutional solid solution is formed. If the foreign atoms are introduced at previously unoccupied sites in the lattice, an interstitial solid solution is formed.

The relative stability of the several solid forms is determined by the equilibrium free energies of the alternatives. A solid solution tends to form when the internal-energy component of the free energy is about the same for the three cases, and the entropy associated with the random character of the solid solution provides a lower free energy for the solid-solution structure.

Although there is no quantitative data on such solid-state properties, these principles are the basis for various rules (involving valence, atomic size, lattice type, etc.) used in practice to predict behavior.

The eutectic temperature is the lowest liquid temperature in a solid-liquid equilibrium diagram in which melting-point lowering occurs. The melting point of a mixture is lowered below the lowest melting point of any of the pure components. Phase-rule relations and mass balances make the composition of the phases invariant and a characteristic eutectic liquid composition is determined under these conditions. The eutectics cited are examples of rather extreme melting-point lowering. The Cs_2MoO_4-MoO_3 system cited in Section 4.3 has a eutectic composition with a lowering of melting point (relative to the mean melting point of the pure components) of 465°C. The CaO-Al_2O_3 system shown in Fig. 4.3 has a eutectic with a melting-point lowering of 910°C. Additions of third (and more) components can lower eutectic points even further. Hence, it appears conceivable that in a complex mixture, very low eutectic combinations may exist. The effects in a practical sense may be mitigated by the dilution of high melting point constituents that are uniformly distributed through the matrix.

For the pure oxides constituting more than 1 wt % of the calcine, the lowest melting point is 733°C (TeO_2). In summary, the calcine melting point may vary over a range as wide as 600 to 1600°C with only a very small fraction of liquid at the lower end of the range and extensive melting at the upper end. For substantial volumes of molten eutectics to form, the original, nearly uniform atomic mixture obtained by the rapid evaporation and calcination of aqueous waste solution would have to undergo major solid-state transformation to "assemble" the low-melting species. Actual melting point curves can be obtained in a practical sense only by experimentation; such curves in turn would greatly depend on kinetic effects associated with solid-state transformations. These transformations are addressed in Section 4.5.3 below.

4.5.3. Sintering and Vitrification

Transformation of the microstructure of solid phases requires atomic mobility. The process resulting in mobility in the solid state is termed diffusion on the atomic scale and sintering on the macro scale. When a liquid component (usually a viscous silicate) is introduced as an agent to promote densification in the firing of a ceramic material, the process is termed vitrification. The practical purpose of both sintering and vitrification is to increase the strength and degree of consolidation of a ceramic material

by increasing the density and concomitantly reducing voidage, porosity, and internal surfaces. When vitrification is complete, the material is glass; this is considered in Section 4.6.1. Recrystallization and grain growth occur concomitantly with sintering. Even partial sintering or vitrification of calcine has a profound practical effect on particle size, density, thermal conductivity, and resistance to leaching or to general dispersion. This means that the properties of calcine are improved by high temperature, either by post-calcination treatment or by overheating in storage.

In ceramic practice, the changes that occur when the temperature is increased during the firing of compact oxide powders are (1) changes in grain size and shape, (2) changes in pore shape, and (3) changes in pore size. During consolidation, the changes in pore shape break down the boundaries that previously existed between separate particles, and the size and volume fraction of pores is reduced; shrinkage results. For any volume of material (in bulk) that melts, the volume decreases, because the volume increase by melting of the solid particles is less than the reduction of the void volume by coalescence of liquid particles. Thus, the net result of sintering is densification.

The driving force for densification by solid-state sintering is the net decrease in free energy accompanying the decrease in surface area. The mechanisms of material transfer in the reduction of internal surface are several: diffusion, vaporization-condensation, plastic deformation, or, in the case of melted material, viscous flow. The relative importance of these mechanisms depends on the particular system and conditions. From ceramic practice, it is known that initial particle size and temperature are the key variables for sintering. The rate of densification is relatively high initially, and falls off with time.

In general, the rate of diffusion increases strongly with tempera-ture, the diffusion coefficient D being proportional to the Arrhenius activation factor, $\exp(-Q/RT)$, where Q is the activation energy. Diffusion is more rapid along grain boundaries, where there is disorder, than within the crystal lattice. Similarly, diffusion in ionic melts and glasses is especially important because in general the diffusion coefficient in the random noncrystalline structure is larger by several orders of magnitude than in a crystalline solid. Thus a small amount of glassy material in a ceramic has a strong influence on the overall diffusion-controlled processes in a multiphase system. A representative range of diffusion coefficients is shown as a function of temperature in Fig. 4.4.[1]

Vitrification is to make "glass-like"--that is, to densify with the aid of a viscous liquid phase. This process occurs in the partial melting (thermal "firing") in the production of commercial silicate ceramics as well as in the complete liquification in the production of glasses. In ceramics manufacture, the silicate component forms the liquid in the ceramic body, and the amount and viscosity of the liquid phase must be such that densification occurs within a reasonable time without the unsupported body deforming under the force of gravity. Upon cooling, the silicate forms the solid "bond" hold-ing the ceramic together. The relative and absolute rates of the two processes, densification and deformation, determine the satisfactory temperature and com-position in ceramic firing practice.
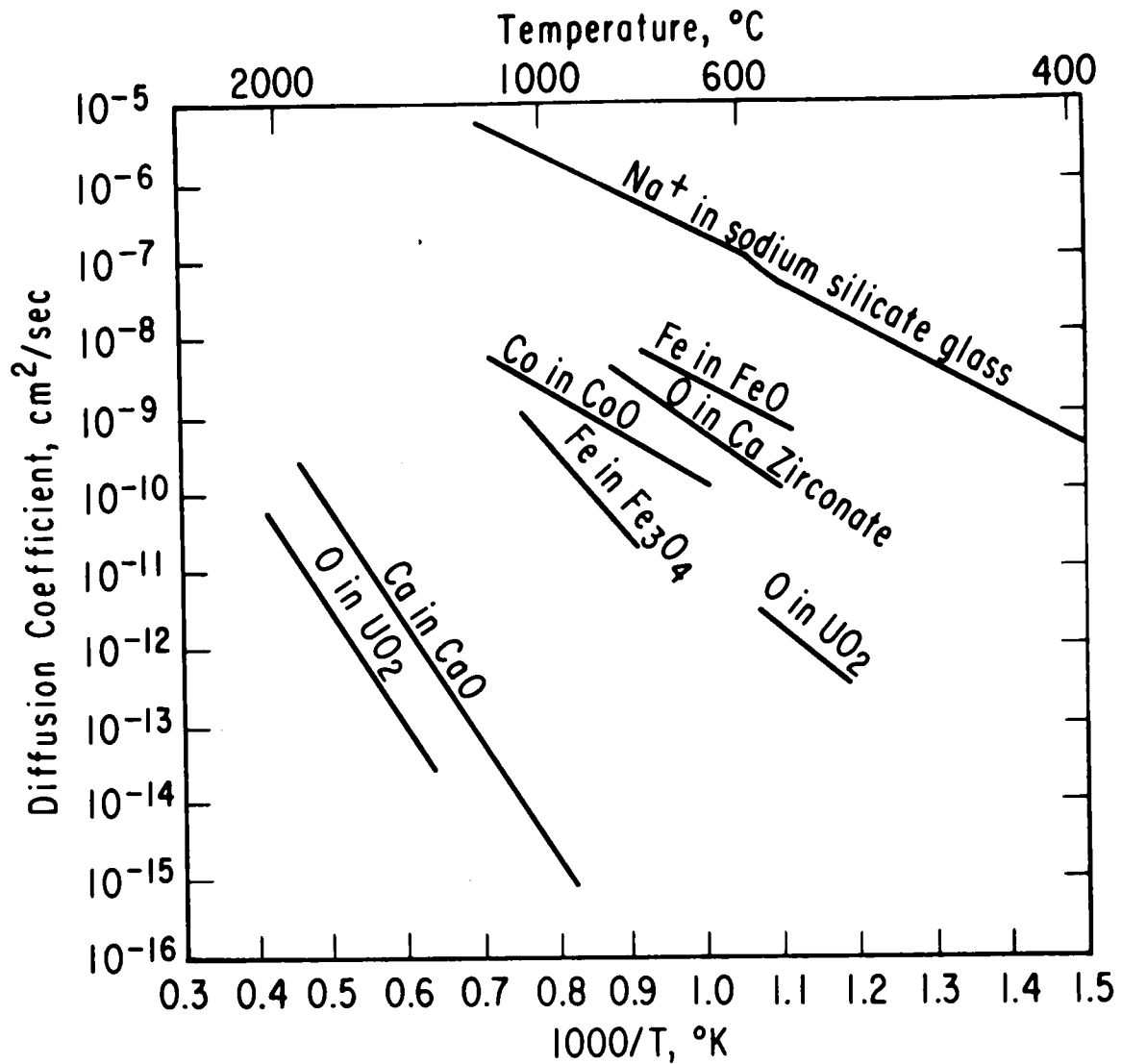
Fig. 4.4. Diffusion Coefficients as a Function of Temperature[1]

The kinetics of densification by vitrification is analyzed similarly to that for solid-state sintering, except that the viscosity and other properties of the liquid phase have the key role, rather than the diffusional processes of the solid phase (as in sintering). The rate of densification by vitrification depends on three major variables: the particle size, viscosity and surface tension of the liquid, and the particle size of the solid, which affects overall consolidation. For silicate systems, the surface tension does not usually vary much with composition. The particle size has a strong effect on the vitrification rate; the rate is increased by a factor of 10 when the particle size is changed from 10 μm to 1 μm. Viscosity has an even more important effect on rate of vitrification. For a typical soda-lime-silica glass, the viscosity decreases by a factor of 1000 for an increase of 100°C, with a corresponding increase in the rate of densification.

Typically, the liquid phase is that of a eutectic, and the fine-grained solid phase allows the entire body to become plastic. The relative amount of liquid and the rate of vitrification are dependent on composition and are highly sensitive to temperature.

Hot pressing is another method of obtaining densification by applying external pressure, rather than depending entirely on the surface energy as a driving force for densification.[1]

4.6. The Nature and Properties of Glass

Glass is defined by the American Association of Testing Materials as "an inorganic product of fusion which has cooled to a rigid condition without crystallizing."[2] This definition implies that glass has no definite melting point, but that its viscosity increases as the temperature is lowered from a fully liquid state. In this section, the major interest is the temperature stability of glass, the properties of glass, and comparisons with alternative (crystalline) forms of the same elements. Typically, the density, thermal conductivity, and coefficient of thermal expansion of glass are lower than those of the ingredient oxides as crystalline solids. Volume-temperature relationships for glasses, liquids, and crystalline solids are illustrated in Fig. 4.5.
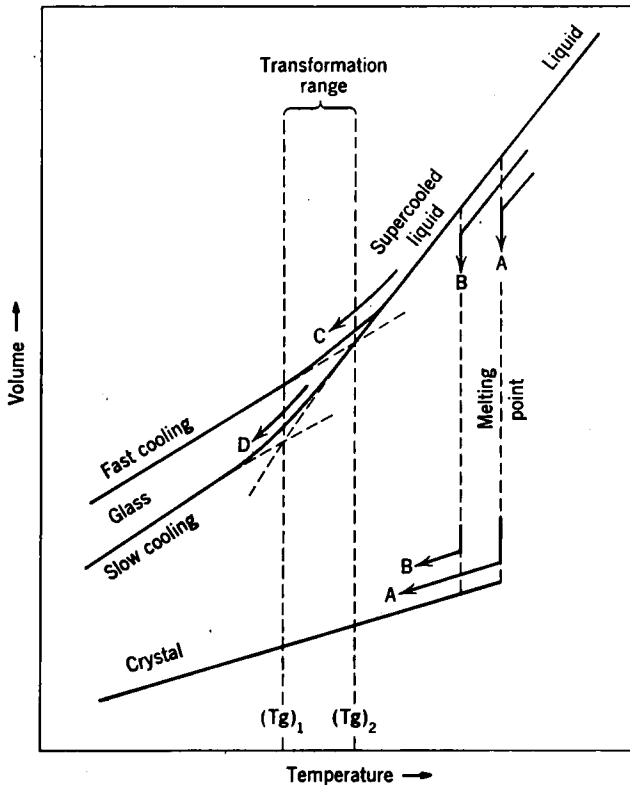
Fig. 4.5.

Volume-temperature relationships for glasses, liquids, supercooled liquids, and crystals.[2]

4.6.1. The Formation and Structure of Glass[1,2]

The noncrystalline structure of glass can be described in relation to crystalline forms of its components by the random network theory. A schematic representation of representative structures illustrating this theory is shown in Fig. 4.6.
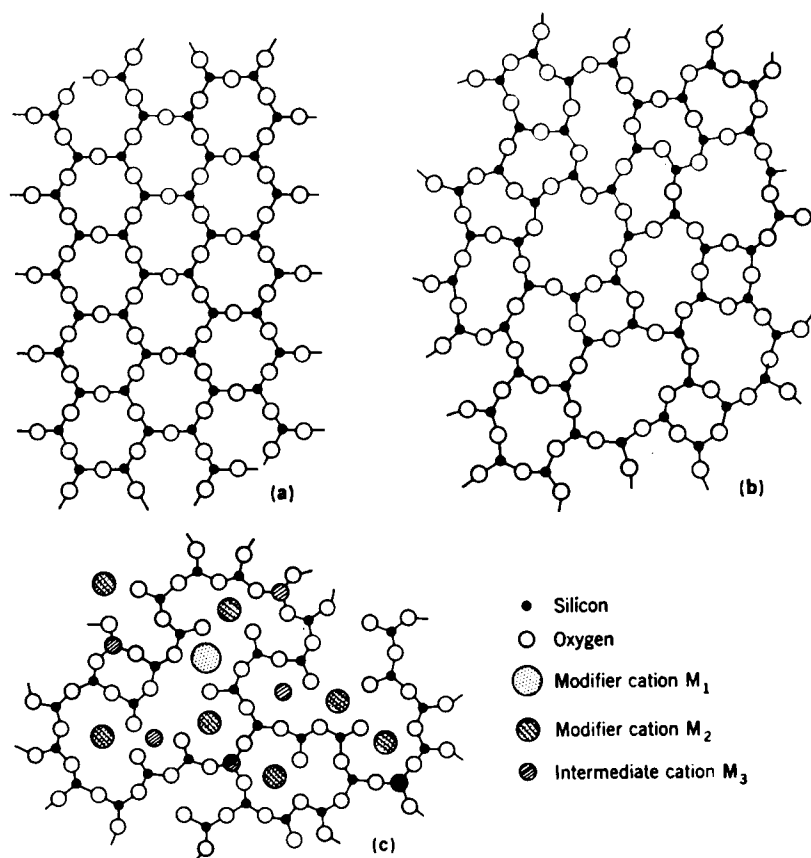
Fig. 4.6. Two-dimensional schematic representation of
(a) a crystalline structure;
(b) a simple glass; and
(c) a multicomponent glass[2]

Although most materials can be prepared in noncrystalline form by rapid cooling from the vapor state to a temperature well below the melting point, most of these structures will revert to crystalline form at any temperature at which the atoms have even a small mobility. Representative silicate glasses, however, have useful noncrystalline stability. Stable oxide glasses form an extended three-dimensional network lacking periodicity (i.e., random) but having energy content comparable to that of the corresponding crystalline network. This essentially requires that the first coordination number of each atom be very nearly the same in the glass as in the crystal. Furthermore, the

second coordination number cannot be a large contributor to the total structure energy. For silica, the difference in structure energy between crystalline crystobalite and vitreous silica is about 1%.[1]

In order to form a stable oxide-glass network, a cation must have a bond strength of about 100 kcal/g-mol. The bond strength is the dissociation energy per g-atom of the cation divided by its coordination number. Such cations can form single-component glasses and are termed "glass formers." Cations with bond strength less than 60 kcal/g-mol do not enter into the network structure (see Fig. 4.6) and are called "modifiers." A group of oxides called "intermediates" do not form glasses themselves but can enter into the network in polycomponent glasses. A summary of elements listed by classification is given in Table 4.4.[1,2]

Of the major fission products, only Zr is a "glass-former." The 1-, 2-, and 3-valence fission products are among the "modifiers." Higher valence elements tend to form binary compounds, e.g., niobates, and their incorporation into glass may be restricted to special conditions. In general, only a "glass-former" can by itself form the three-dimensional random network. Glass-network structuring tends to be covalent, e.g., the silicon-oxide bond. "Modifiers" tend to bond ionically to the anions in the network and are used to alter properties. An intermediate can enter into a glass-forming position or into a modifying position in a complex glass.[2]

The common oxides of glass may also be classified as "glass formers," "stabilizers," and "fluxes." Glass formers are as defined above. Fluxes (e.g., Na_2O, K_2O, and B_2O_3) are added to lower the melting and working temperatures by decreasing viscosity. Stabilizers are added to improve chemical durability or to prevent crystallization[2] (e.g., CaO, MgO, and Al_2O_3).

An example of a stabilizer is alumina. When it is added to an alkali silicate glass, a "hardening" is observed. Alumina also improves chemical durability and resistance to devitrification. Alkaline earth aluminosilicates form the basis for glasses requiring high temperatures of use. Aluminosilicate glasses find use in top-of-stove ware, fiberglass, and glass-ceramics.[2]

If it is desired to densify waste calcine by vitrification, a "frit" can be mixed with the calcine and the temperature can be increased to form the vitreous liquid phase. The frit can consist of SiO_2 and possibly B_2O_3. If cation additions are desirable, Al_2O_3 or ZrO_2 would be preferable to Na_2O or K_2O for high service temperatures, but alkali metal oxides would allow vitrification at low temperatures.

Although an analysis of glass-making is outside the scope of this summary of chemical properties relevant to canister containment, the effect of frit additions on the solid-liquid equilibria discussed earlier in this section is next discussed generally. In Fig. 4.7 are shown equilibrium diagrams of the systems $SrO-ZrO_2$, $SrO-SiO_2$, $Nd_2O_3-SiO_2$, and $B_2O_3-SiO_2$. The eutectics of the two systems containing strontium show that the silicate system has a liquid phase at a temperature about 340°C lower than the zirconate system. It is expected that the neodymium-silicate system would be representative of the large rare earth component of the fission products; its eutectic is about 700°C lower than the melting point of pure Nd_2O_3. A low-temperature liquid

TABLE 4.4. Coordination Number and Bond Strength of Oxides[1,2]

	M in MO_z	Valence	Dissociation Energy per MO_z (kcal/mole)	Co-ordination Number	Single-Bond Strength (kcal/mole)
Glass formers	B	3	356	3	119
	Si	4	424	4	106
	Ge	4	431	4	108
	Al	3	402–317	4	101–79
	B	3	356	4	89
	P	5	442	4	111–88
	V	5	449	4	112–90
	As	5	349	4	87–70
	Sb	5	339	4	85–68
	Zr	4	485	6	81
Intermediates	Ti	4	435	6	73
	Zn	2	144	2	72
	Pb	2	145	2	73
	Al	3	317–402	6	53–67
	Th	4	516	8	64
	Be	2	250	4	63
	Zr	4	485	8	61
	Cd	2	119	2	60
Modifiers	Sc	3	362	6	60
	La	3	406	7	58
	Y	3	399	8	50
	Sn	4	278	6	46
	Ga	3	267	6	45
	In	3	259	6	43
	Th	4	516	12	43
	Pb	4	232	6	39
	Mg	2	222	6	37
	Li	1	144	4	36
	Pb	2	145	4	36
	Zn	2	144	4	36
	Ba	2	260	8	33
	Ca	2	257	8	32
	Sr	2	256	8	32
	Cd	2	119	4	30
	Na	1	120	6	20
	Cd	2	119	6	20
	K	1	115	9	13
	Rb	1	115	10	12
	Hg	2	68	6	11
	Cs	1	114	12	10

SrO–ZrO₂

SrO-ZrO$_2$ phase diagram

Temperatures: 2500, 2000, 1500, 1000

Liquid

SrZrO$_3$+Liq.

Sr$_4$Zr$_3$O$_{10}$+Liq.

Liq.+SrO

SrZrO$_3$ + Sr$_4$Zr$_3$O$_{10}$

Sr$_4$Zr$_3$O$_{10}$+SrO

Sr$_4$Zr$_3$O$_{10}$

SrZrO$_3$+Sr$_3$Zr$_2$O$_7$

Sr$_3$Zr$_2$O$_7$

Sr$_3$Zr$_2$O$_7$ + SrO

Sr$_2$ZrO$_4$

SrZrO$_3$ + Sr$_2$ZrO$_4$

Sr$_2$ZrO$_4$ + SrO

SrZrO$_3$ + SrO

50 55 60 65 70

SrZrO$_3$ SrO (Mol. %) SrO →

← ZrO$_2$
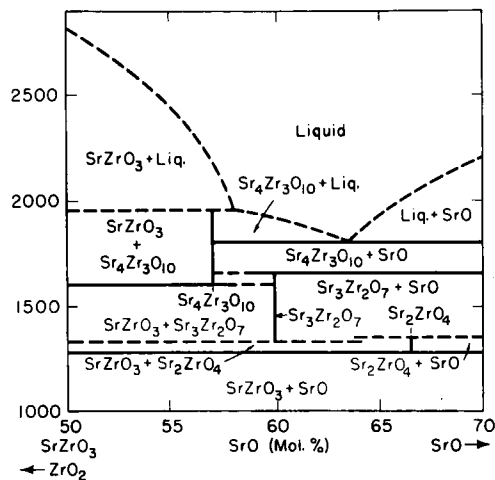
System SrO–SrZrO₃ [14]

SrO–SiO₂

Temperatures: 1700, 1500, 1300

Liquid B

Liquids A & B

2SrO·SiO$_2$+Liquid B

SrO·SiO$_2$+Liquid B

Cristobalite & Liquid A

SrO+2SrO·SiO$_2$

1545°

1580°

Cristobalite & Liquid B

2SrO·SiO$_2$ +SrO·SiO$_2$

SrO·SiO$_2$ +Liquid B

1470°

Tridymite & Liquid B

1358°

SrO·SiO$_2$+Tridymite

0 20 40 60 80 100

SrO 2SrO·SiO$_2$ SrO·SiO$_2$ SiO$_2$
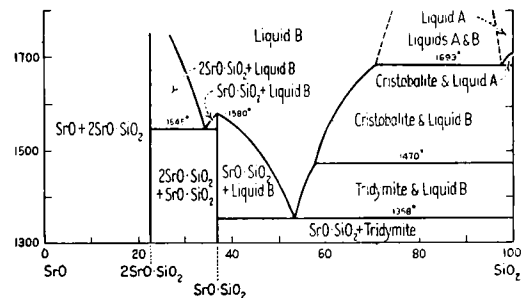
System SrO–SiO₂ [13]

Nd₂O₃–SiO₂

Temperatures: 2300, 2200, 2100, 2000, 1900, 1800, 1700, 1600, 1500

Liquid

Nd$_2$O$_3$·SiO$_2$+Liq.

2Nd$_2$O$_3$·3SiO$_2$+Liq.

1980° 1960°

Nd$_2$O$_3$·2SiO$_2$ + Liq.

Nd$_2$O$_3$ + Liq.

1830°

1750°

Two Liquids

SiO$_2$+Liq.

1:1 + 2:3

2:3 + 1:2

1680°

1660°

1600° SiO$_2$+Liq.

Nd$_2$O$_3$ +Nd$_2$O$_3$·SiO$_2$

Nd$_2$O$_3$·2SiO$_2$+SiO$_2$

Nd$_2$O$_3$ 20 40 60 80 SiO$_2$

1:1 2:3 1:2

Mol. %
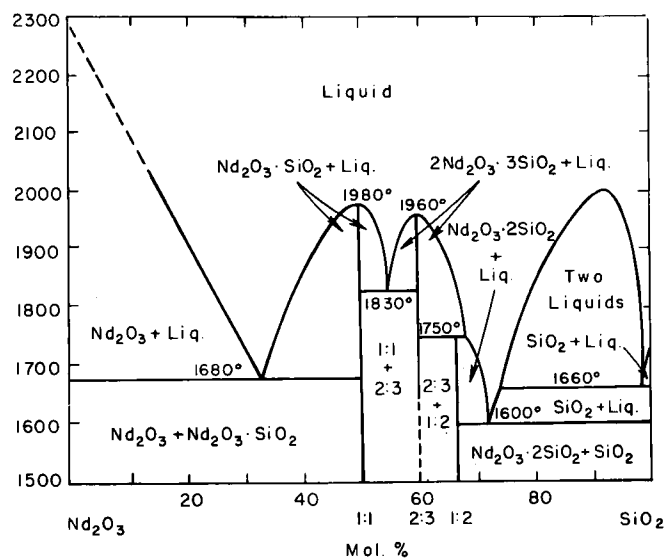
**System Nd₂O₃–SiO₂. Oxide ratios
of compounds are given as
Nd₂O₃:SiO₂** [14]

B₂O₃–SiO₂

Temperatures: 1600, 1200, 800, 400, 0

Cristobalite + Liquid

Tridymite + Liquid

Liquid

Quartz + Liquid

Quartz + B$_2$O$_3$

SiO$_2$ 20 40 60 80 B$_2$O$_3$
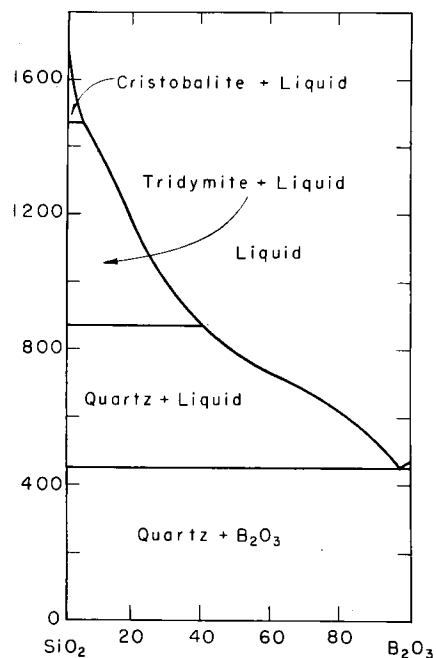
System B₂O₃–SiO₂ [14]

**Fig. 4.7.   Phase Diagrams Illustrating Melting Point Lowering
in Vitrification**

phase is associated with the $B_2O_3-SiO_2$ system; its eutectic is at about 430°C. Since no compounds are formed in this binary system, the potential for glass formation would predominate, even though in this diagram only the equilibrium crystal states are considered. If conversion of calcine to a consolidated monolithic form were the objective, a $SiO_2-B_2O_3-K_2O$ frit could possibly accomplish this at temperatures below 1000°C. The development of waste glass compositions at PNL is continuing on a systematic basis, guided by the overall objectives of the waste management program.

A new field of glass technology, the conversion of glass to fine-grained glass ceramics (more than 50% crystalline) is based on heterogeneous nucleation and crystal growth.* This process is made possible by the use of a minor ingredient (the nucleating agent) which can be precipitated as a crystal or immiscible liquid in concentrations as high as 10^{15} nuclei/mm^3 of glass. Crystallization occurs at a temperature at which these minor phases can cause the major crystal phases of the glass to nucleate and grow. Dimensional change during this treatment is about 1-2%, depending on composition, time, and temperature. Zirconium dioxide and titanium dioxide are among the nucleating agents.[2]

4.6.2. Properties of Glass

4.6.2.1. Thermal Expansion

Since glass does not yield or deform significantly at room temperature, a careful consideration of its thermal expansion characteristics is necessary in order to use it successfully in a composite structure with other materials.[2] For the purpose of our preliminary analysis, we have assumed for glass the well-established properties of commercial Pyrex (Corning 7740). The coefficients of thermal expansion of glasses and glass-ceramics vary widely. A presentation of thermal expansions of typical materials of interest is shown in Fig. 4.8. Included in the figure for illustrative purposes is the approximate curve for the expansion of a simulated PNL waste glass, and the expansion coefficient of Al_2O_3 as representative of a crystalline ceramic. The references cited in the figure caption should be consulted for details.

4.6.2.2. Viscosity

The rigidity of glass at elevated temperature requires special consideration, since glass does not have a definite melting point. Some representative glasses are characterized by viscosity in Table 4.5.

The viscosities are listed for a borosilicate glass (Pyrex), a nearly pure silica glass (96% silica, quartz-like), and an aluminosilicate glass manufactured by Corning. In the practical property column, the lowest viscosity (highest fluidity) condition is listed at the top, and viscosity increases as one proceeds downward. A practical characterization of the viscosity is provided in the table by some descriptive terms used in glass manufacture. The "strain point" is the lowest temperature at which there is practical stress relief in short time periods (hours). The "upper use temperature" is the approximate temperature range in which the (annealed)

---

* This subject is discussed in Section 4.7.
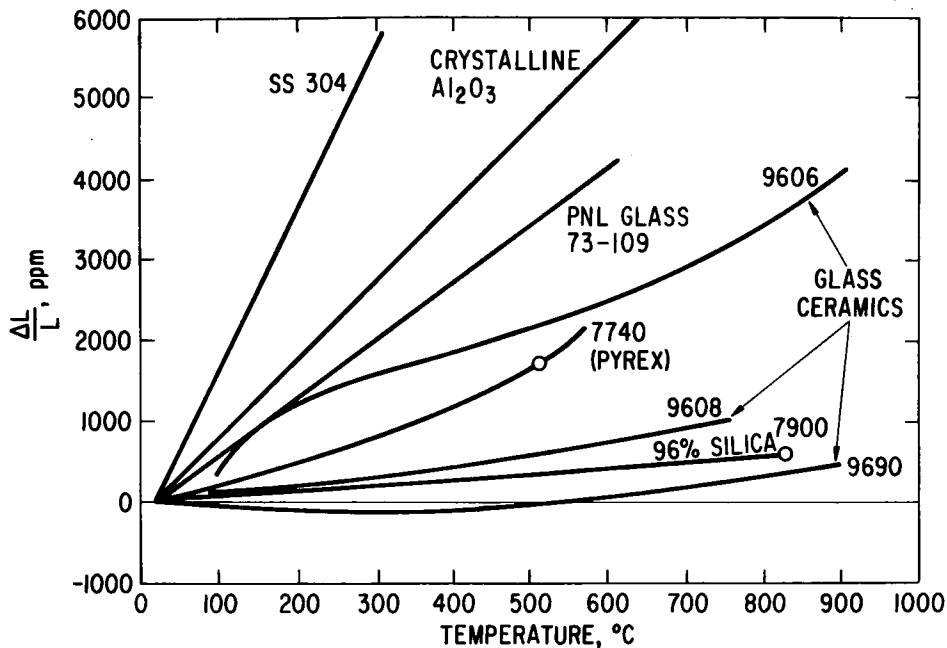
Fig. 4.8. Expansion Characteristics of Selected Glass Ceramics,[12]
Stainless Steel,[12] and Al_2O_3 Crystalline Ceramics.
(Note added lines for SS304 (smoothed) and a
simulated glass, 73-109, by PNL[13])

glass is subject to softening and deformation. In this range also, the glass
is vulnerable to damage by thermal shock under rapid cooling. The higher the
melting and softening points of the glass, the higher is the temperature at
which long-term flow can reduce stresses; these properties depend on composition
and the state of vitrification. A glass-ceramic[14] (Corning "Pyroceram" radomes
for ballistic missiles) has a softening point of 1350°C, 500°C higher than the
Pyrex (borosilicate glass) listed in Table 4.5.

4.6.2.3. Other Properties

Thermal conductivities adopted as reference conditions
are 0.20 Btu/(hr)(ft)(°F) [0.35 W/(m)(°C)] for calcine and 0.60 for glass. The
lower value for calcine is due to its unconsolidated nature (high void frac-
tion). Equivalences in various units for our reference case and representa-
tive other materials are given below.

	Thermal Conductivity at 100°C		
	Btu/(Hr)(ft)(°F)	cal/(sec)(cm)(°C)	W/(cm)(°C)
reference calcine	0.20	0.00083	0.0035
reference glass	0.60	0.0025	0.0105
Pyrex glass (7740)	0.73[2]	0.0030[2]	0.0126[2]
Fused quartz glass	0.97[2]	0.0040[2]	0.0167[2]
Al_2O_3 (crystalline ceramic)	17.4[1]	0.072[1]	0.301[1]
$UO_{2.00}$	5.8[1]	0.024[1]	0.100[1]
Glass-ceramic (9606)	2.08[2]	0.0086[2]	0.036[2]

TABLE 4.5. Viscosity of Representative Commercial Glasses[2]

Practical Property	Viscosity (poises)	Temperature (°C)		
		Pyrex[a]	96% Silica[b]	Alumino-silicate[c]
Melting Range	50 to 500	---	---	---
"Melting Point"	100	---	---	---
Pressing Range	500 to 7000	>1300	---	>1200
"Working Point"	10,000	1245	---	1190
Blowing and Drawing Range	1×10^4 to 1×10^5	>900	>1600	>1100
"Flow Point"	1×10^5	>900	>1600	>1000
Softening Range	3×10^7 to 1.5×10^8	>820	>1500	>915
"Softening Point"	3×10^7	820	1500	915
"Annealing Point"	1×10^{13}	565	910	715
"Strain Point"	3.2×10^{14}	515	820	670
"Upper Use Temperature,"				
"Extreme"	$\sim 10^{15}$	490	1100	650
"Normal"	$>10^{16}$	230	800	200

[a] Corning type 7740[2]

[b] Corning type 7900[2]

[c] Corning type 1720[2]

In general, regular crystalline forms have higher thermal conductivity than do solid solutions or glasses. Thermal conductivity of the above materials (and oxides in general) decreases as the temperature increases. For example, pure alumina has at 1000°C only one-fifth the thermal conductivity shown above for 100°C. The thermal conductivity of silica glass, on the other hand, increases by 25% over the same[11] temperature range. However, at 1000°C the thermal conductivity of this glass is still only about 40% of that of crystalline alumina and at 100°C about 8% of that of alumina.

Densities of commercial borosilicate, alumino-silicate, alumino-borosilicate glasses, and glass ceramics range from 2.16 to 2.52 g/cm^3, somewhat lower than those of the corresponding crystalline materials. Because the reference waste glass is composed of heavier fission product elements, it has a density of 3.5 g/cm^3.

The corrosiveness of glass to container materials depends on the temperature. A mobile liquid phase would dissolve the protective oxide coating of common structural metals such as stainless steel, and the chemical attack on the exposed metal would depend on the oxidative potential of the molten phase. A temperature low enough to reduce the mobility of the

glass below that capable of agressive attack would be expected to lie between the "softening point" and the "strain point" of the viscosity, defined for commercial glasses in Table 4.5. Since the diffusion rates for glass phases are one order of magnitude higher for glass than for crystalline materials, the safe temperature (without specific tests) would be at the lower temperatures of this 515-820°C range for Pyrex, which has a "flow point" of about 900°C.

In commercial glass manufacture, most of the forming steps are carried out at temperatures where glass is easily deformed plastically but where it is viscous enough not to need containment as a liquid. Iron and steel are widely used. For liquid glass containment and other special functions, refractory ceramics are used. Refractories having use temperatures above 1400°C are composed of Al_2O_3, SiO_2, and MgO.[2]

4.7. Nucleation, Crystal Growth, and Devitrification[1,2]

The concern for nucleation in this study is confined to transformations of glass by recrystallization. All glass is unstable with respect to one or more crystalline compounds. The practical stability of glass, that is, its resistance to spontaneous nucleation, is due to the fact that nucleation rates are significant only at temperatures below those at which high rates of crystal growth occur. The temperature displacement of nucleation and crystal growth rates is shown diagrammatically in Fig. 4.9, where rates are plotted against the temperature of undercooling $(T_L - T)$, where T_L is the liquidus temperature. For glasses highly resistant to homogeneous nucleation, the curves would be more widely separated.

The extent of devitrification is the result of a competition of (a) the thermodynamic driving force (free energy of formation of crystal phase), which increases with $(T_L - T)$ and (b) a diffusion rate for crystal growth, which decreases with $(T_L - T)$. This competition applies to both the nucleation and the crystal growth curves and results in their separate maxima.[2]

In general, the rate of growth of crystals from silicate glasses becomes negligible at a temperature about 250°C below the liquidus. For most glasses, this undercooling temperature is still above the annealing range and above the nucleation temperature and provides no problems for normal glass manufacture and use. However, when glasses are held above the transition (nucleation) range for long periods of time, devitrification takes place. The maximum rate of growth of individual crystals in these systems is of the order of 1 mm/hr, but this rate is seldom reached in silicate glasses.[1] The rapid and controlled nucleation in glass-ceramic manufacture requires heterogeneous nucleation.

The nucleating agent in glass-ceramic practice (as cited in the Section 4.6.1) is typically TiO_2. Titania is soluble in borosilicate glasses at about 1100°C. On cooling to about 750°C, there is a high degree of super-saturation, and nucleation sites form in the glass. When the glass is reheated to temperatures that allow crystal growth, it is transformed into a ceramic having the same shape and size as the original, but nearly 100% crystalline. It is stronger, has more impact resistance, and has improved thermal conductivity and higher temperature serviceability.
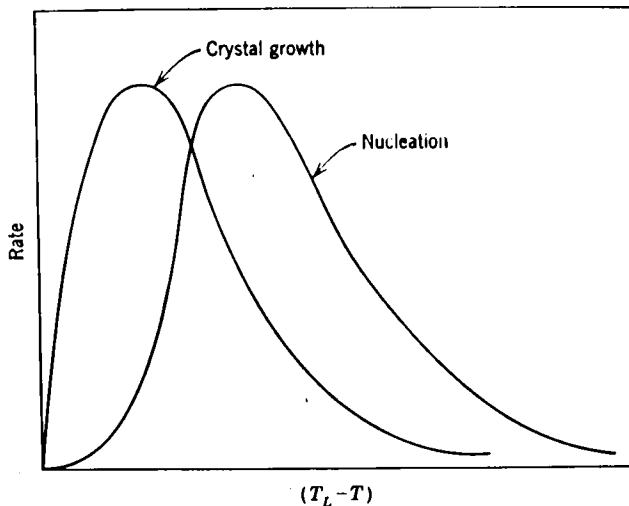
Fig. 4.9. Nucleation and crystal growth rates as a function of undercooling.

The kinetics of devitrification, homogeneous or heterogeneous, cannot be predicted quantitatively because of the complexity and the lack of basic data, even though the diffusion can be estimated (according to the Stokes-Einstein relationship) by its inverse proportionality to the viscosity, which is readily obtained for glasses.[1]

In practical terms, the chemical stability of glass is uncertain for extended time exposure at elevated temperatures. If the volume change of devitrification is small (so that no strains develop), the effect of devitrification may be to improve the thermal properties. In particular, the melting point or corrosivity toward the canister is not likely to be adversely affected. Devitrification results in an increase of leachability of glass in water. However, the nearly void-free, microcrystalline material, composed of low-solubility compounds, is not expected to show a major increase in leachability, *i.e.*, no more than about a factor of 10.

4.8. Summary of Aspects of Material Chemistry of Solid Waste with Respect to their Influence on Reliability of Canister Containment

The degree of stability and inertness of the solid waste can be directly related to the chemistry of the waste material, starting from the point of the origin of the waste as an aqueous nitrate solution through its storage lifetime. The criterion for chemical stability and inertness is that the waste shall not subject the canister to appreciable mechanical stress and/or chemical corrosion in storage conditions. The chief requirement is control of temperature during storage and handling by removal of the heat generated by radioactive decay. Other requirements concern final preparation of waste solid at the time of sealing the waste in the canister: (a) the removal of residual reagents and certain fission products which could be significantly volatile or corrosive in storage, and (b) the constitution of the final waste in a form which is stable in terms of the containment criteria stated above.

For the stored waste form, reliable containment is determined by the temperature control and by the behavior of the waste at whatever temperature (normal or abnormal) is encountered in storage. The waste composition and

structure, the temperature behavior, and the interaction with the canister material have been reviewed in this section from the standpoint of the chemistry of the materials. Chemical properties are summarized below with respect to the major items relevant as factors affecting reliability. In the list of factors below, the ones that are more specific and quantitative in terms of our discussion of material chemistry are stated first. The others of more general and strategic import follow in the list.

a. Maximum internal gas pressurization as a function of residual nitrate and water composition of calcine, void fraction of calcine, and temperature.

b. Temperature range of melting or sintering of calcine as a function of calcine composition and formation.

c. Viscosity of glass as a function of glass composition and temperature.

d. Specific fission products having the greatest tendency for migration in the calcine as a function of temperature.

e. Temperatures at which levels of residual nitrate and water in calcine may be reduced by thermal decomposition prior to sealing of the canister.

f. Temperature coefficients of thermal expansion of waste solids, relative to that of canister metal and their effect on the development of stress in the canister.

g. Volume changes of waste solid as a function of temperature and composition that may generate stresses in the canister.

h. Oxidation potential of calcine as a function of the chemical conditions of calcination (calcine formation with valences higher than four tend to form volatile species of fission products with decreasing stability at higher temperatures).

i. Chemical aggressiveness to canister metal of calcine and glass as a function of temperature, oxide diffusion rates, plasticity or viscosity of solid, and waste composition.

j. Range of effects of overheating, internally or at the canister wall, for calcine and glass.

k. Basis of devitrification of glass and its effect on solid waste properties.

l. Basis of increasing the density and thermal conductivity by sintering and/or vitrification (by the addition of frit).

m. The degrees of homogeneity and monolithicity of the solid waste and the importance of their effect on the properties of the solid.

These chemical factors that are related to reliability have been discussed in the above parts of Section 4 and are considered in later sections of this report in assessing the potential damage to the canister and the control methods for achieving overall reliability. In practice, the fission product oxides in waste calcine become more "refractory" and "stable" by exposure to high temperatures (of the order of 700°C). This makes them "easy" to store. On the other hand, strict temperature limits have to be imposed on the canister in all operations because of adverse effects on the metal. The above general evaluation of temperature behavior is not needed to ensure reliability where reference temperatures are assured, but are needed to assess abnormalities, temperature control requirements, and system optimality.

Reference for Section 4

1. W. D. Kingery, Introduction to Ceramics, Wiley and Sons, Inc. New York (1960).

2. J. R. Hutchins and R. V. Harrington, Glass, Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 10, pp. 533-604, 2nd ed. (1966).

3. W. F. Bonner (PNL), private communication to W. B. Seefeldt (ANL) (January 24, 1975), Attachment, Radioactive Wastes After Conversion to Calcine.

4. Oak Ridge National Laboratory, Siting of Fuel Reprocessing Plants and Waste Management Facilities, ORNL-4451 (July 1970).

5. Lange's Handbook of Chemistry, 11th Ed., (1973).

6. A. Glassner, The Thermochemical Properties of the Oxides, Fluorides, Chlorides to 2500°K, ANL-5750 (October 1965).

7. F. M. Perel'man, Rubidium and Cesium, Pergamon Press (1975).

8. E. M. Levin et al., Phase Diagrams for Ceramicists, The American Ceramic Society, p. 86 (1964).

9. C. E. Johnson et al., Chemical Engineering Division, Fuels and Materials Chemistry Annual Report, July 1973-June 1974, ANL-8122, p. 39 (January 1975).

10. A. A. Jonke, N. M. Levitz, E. J. Petkus, and R. G. Taecker, Fluidized-Bed Process for the Production of Uranium Tetrafluoride from Uranyl Nitrate, Interim Report, ANL-5363 (December 30, 1954).

11. W. A. Ross, Pacific Northwest Laboratories, private communication (1975).

12. Battelle Pacific Northwest Laboratories, Quarterly Progress Report Research and Development Activities: Waste Fixation Program, April through June, 1974, BNWL-1841 (July 1974).

13. E. M. Levin et al., op. cit., p. 119

14. E. M. Levin et al., Phase Diagrams For Ceramicists, 1969 Supplement (Figures 2067-4149), The American Ceramic Society (1969).

5. CHARACTERISTICS OF CANISTERS

5.1. General

Containment of high-level radioactive waste in retrievable canisters imposes a basic requirement that the canister material be inert to both the internal and external environment of the canister and have resistance to deformation and rupture under mechanical stress imposed in any of the operations, including filling, transport, and storage. Only a high-strength, ductile, corrosion-resistant metal is likely to have these properties. A two-metal composite may be satisfactory for a wide range of exposure conditions, but it is also likely that a single alloy would be satisfactory, and at lower cost. The established state-of-the-art of mechanical and corrosion properties for a wide range of steels, including stainless steel, is the basis for selection of canister material.

The reference material of construction for the waste canister is austenitic stainless steel type 304L. Because state-of-the-art materials have similar mechanical properties and because basic corrosion principles apply, our focus on 304L has the advantage of constituting a reference without preventing consideration of other alloys if a clear basis for a different material is evident.

5.2. Reference Properties of Stainless Steel

Reference properties of the stainless steels used in this discussion are summarized in Table 5.1. Nominal tensile properties are summarized in Table 5.2. Creep and rupture data are given in Table 5.3. Elevated-temperature

TABLE 5.1. Properties of Stainless Steel Type SS304 and 304L

Melting Range: °F [°C]	2550-2650 [1399-1454]
Specific Heat 32-212°F (0-100°C): Btu/(lb)(°F)[J/(kg)(°C)]	0.12 [502.4]
Thermal Conductivity, 212°F (100°C): Btu/(hr)(ft^2)(°F/ft)[W/(m)(°C)]	9.4 [16.3]
Coefficient of Thermal Expansion, 32-1200°F (0-649°C): °F^{-1} [°C^{-1}]	10.4 x 10^{-6} [18.7 x 10^{-6}]
Modulus of Elasticity: psi [N/m^2]	28 x 10^6 [1.93 x 10^{11}]
Modulus of Rigidity: psi [N/m^2]	12 x 10^6 [8.62 x 10^{10}]
Density: lb/in.^{3} [g/cm^3]	0.29 [8.03]

strength as a function of temperature is shown in Fig. 5.1, and the effect of cold work on the yield strength is shown in Fig. 5.2. It should be noted that for the nominal properties shown above, individual production lots of SS304L vary considerably. Also, some variation may be expected within a lot.

TABLE 5.2. Nominal Tensile Properties of Stainless Steels 304 and 304L[1]

Form and Condition	Yield Strength, (0.2% Offset) (ksi)[a]	Tensile strength (ksi)[a]	Elongation (2 in.) (%)	Reduction of area (%)	Rockwell Hardness
Type 304					
Sheet and Strip					
Annealed	42	84	55	–	B80
Bars					
Annealed	35	85	60	70	–
Cold drawn	60-95	100-125	60-25	–	–
Wire					
Annealed	35	90-105	60[b]	65	B83
Soft temper	60-90	100-125	45[b]	65	B95
Hard temper	105-125	140-160	25[b]	55	C33
Type 304L					
Sheet and Strip					
Annealed	39	81	55	–	B79

[a] ksi = 10^3 psi = thousands of lb/in.^{2}

[b] Gage length = 4 x diameter

TABLE 5.3. Creep and Stress-Rupture Properties of
Annealed Wrought Stainless Steel Type 304[1]

AISI type	Test temperature, °F (°C)		Stress (ksi)[a] for creep rate of		Stress (ksi) for rupture in 100 hr
			0.00001 %/hr	0.0001 %/hr	
304	1000	(538)	12	20	47
	1200	(649)	4	8	23
	1500	(815)	1	2	7

[a] To convert ksi to N/m^2, multiply by 6.895 x 10^6.

Yield strengths for 304L vary from 20,000 psi to 50,000 psi (1.38 x 10^8 to 3.45 x 10^8 N/m^2). Yield stresses at elevated temperature, shown in Fig. 5.3, illustrate the wide variability of the data.[2]

5.3. Variations in Properties and Basis for Quality Control Considerations

In subsequent sections on stress analysis and corrosion behavior of canisters, the importance of specific properties and specifications of stainless steel is discussed. For example, in a certain range of elevated temperatures, carbide may precipitate in the grain boundaries. This phenomenon is termed sensitization, and it leads to increased susceptibility to certain kinds of
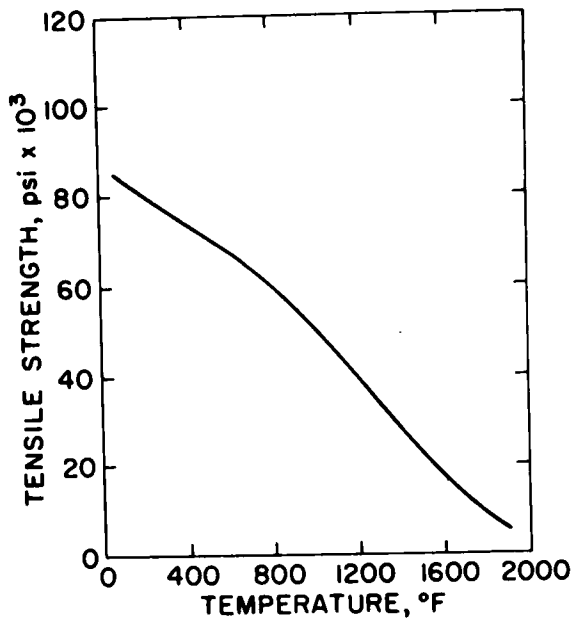
Fig. 5.1. Short-time Elevated-
Temperature Tensile Strength
of Stainless Steel 304[1]
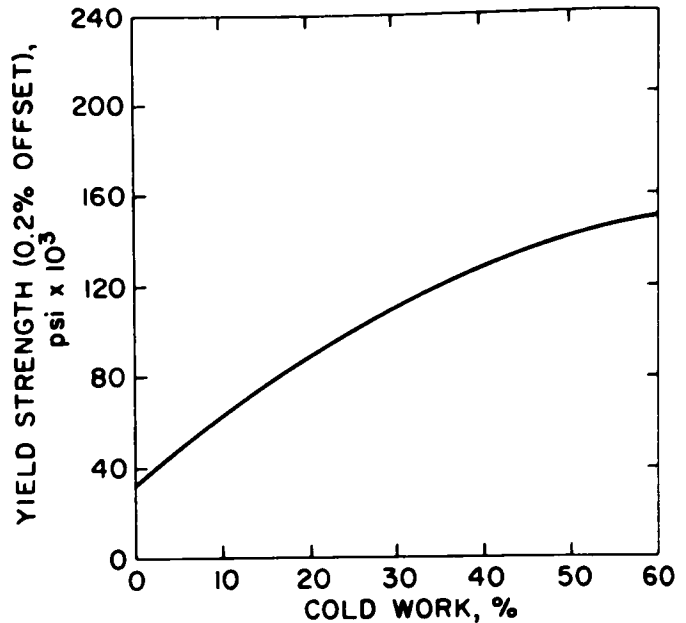
Fig. 5.2. Effect of Cold Work on
the Yield Strength of Stainless
Steel 304[1]

corrosive attack of austenitic stainless steel type 304. The reference alloy
304L has a lower carbon specification than 304 and this reduces the potential
for sensitization. The question of whether low carbon specifications are
uniformly met for steel for individual canisters or lots of canisters is a
matter of standards and quality control. The degree of uniformity of all
portions of canister material with respect to all major properties is an
important consideration.

The properties of material nominally of type 304L vary considerably. A
study of the creep and tensile properties of 20 heats of type 304 steel showed
significant departures from standard behavior on reannealing (stress relief),
including 100-fold variations of minimum creep rates and ∿10-fold variations
to rupture. The primary specifications of mechanical strength and ductility
were well met.[2]

In its general strength, ductility, and resistance to highly corrosive
environments, 304L is well qualified and perhaps even overqualified. Because
of its possible exposure to high temperatures during filling and its long-term
exposure to water environments under stress, the capability of assuring that
certain properties conform to specification will have to be carefully evaluated.

5.4. Fabrication, Testing, and Closure of Canisters

Fabrication, testing, and closure of canisters are described in Sections
3.1 and 3.3.

Canister dimensions and heat loadings for reference conditions are

described in Section 3.7.

Reliability considerations of systems design are also discussed in Section 8.
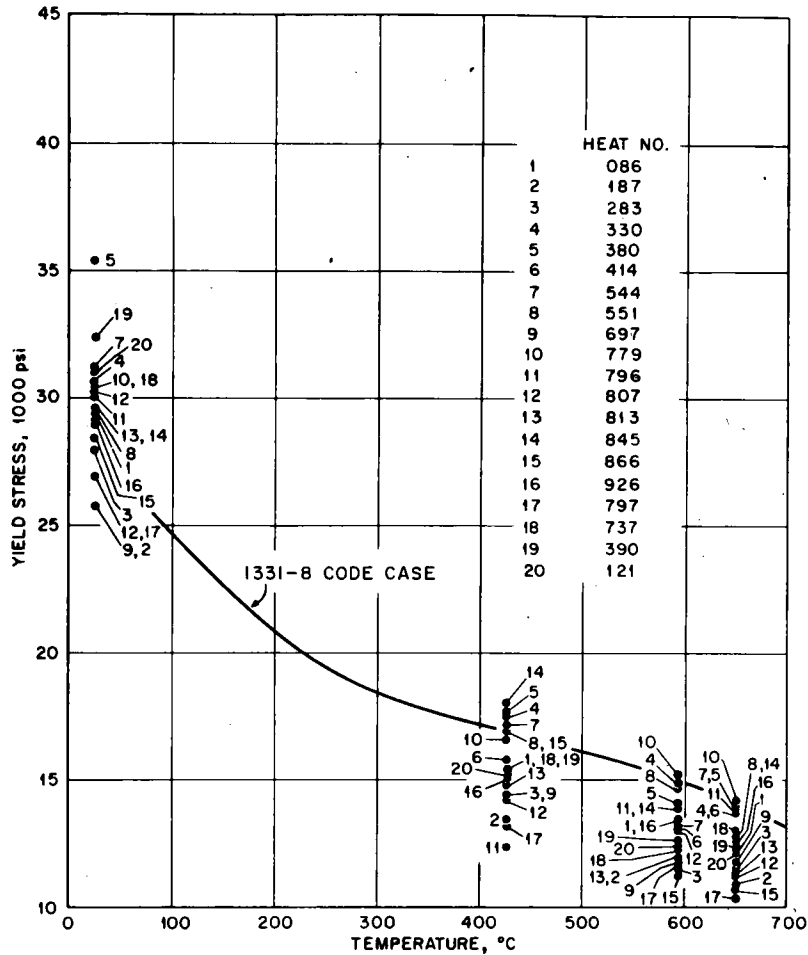
Fig. 5.3.   Comparison of the Observed Yield Stresses of Re-annealed
            (9.5 hr at 1065°C, 1950°F) Type 304 Stainless Steel
            with Minimum Yield Stresses from ASME Code Case 1331-8.
            1000 psi = 6.895 MPa.

Reference for Section 5

1. J. L. Everhart, <u>Engineering Properties of Nickel and Nickel Alloys</u>, Plenum Press, New York (1971).

2. H. E. McCoy, <u>Tensile and Creep Properties of Several Heats of Type 304 Stainless Steel</u>, ORNL-TM-4709 (November 1974).

6. CONDITIONS AND METHODS OF CONTROL OF INTERNAL ATTACK

6.1. Development of Canister Stresses Due to Pressurization from Decomposition of Residual Nitrates and Volatilization of Residual Water in Calcine

High-level radioactive waste emerges from the Purex processing of spent reactor fuel as a nitric acid solution. Primary solidification of this high-level waste is accomplished by evaporation and calcination to form a dry solid product, consisting mainly of fission product oxides. Residual nitrate and water, which may be present to the extent of 0.5% by weight[1] after primary calcination, may have effects that are adverse to stainless steel. Experience at the ICPP suggests that the nitrogen content (expressed as N_2O_5) and the water content of their waste calcine is of the order of one percent for each.[2] At temperatures higher than those encountered during calcination, nitrate and water may form gaseous products by decomposition and desorption that could result in high internal pressures that would be expected to produce stresses in the sealed containers.

6.1.1. General Features of the Problem

A model for the calculation of potential pressures from further denitration and dehydration of calcine containing residual nitrate and water was described in Section 4.4. The potential pressure generated is

$$P(atm) = 9.26 \ T \left(\frac{1 - y}{y}\right) \ x + 18.23 \ T \left(\frac{1 - y}{y}\right) z \tag{1}$$

where

      T = temperature of the gas space, °K
      y = void fraction of canister
      x = weight fraction of nitrate in calcine
      z = weight fraction of water in calcine

In the above expression for P(atm), the first term is the pressure due to nitrate decomposition and the second term that due to dehydration. As an illustration of the pressure for particular values, consider $y = 0.7$, $x = 0.015$, and $z = 0.005$. For this case,

$$P(atm) = 0.0986 \ T(°K) \tag{2}$$

The pressure is 36.8 atm at 100°C, 66.4 atm at 400°C, and 106 atm at 800°C. The significance of these pressures may be seen by comparing them to the pressure which would stress stainless steel to the yield point, *i.e.*, a stress of about 30,000 psi (2040 atm). In general, the circumferential tensile stress (S, psi) in a thin-walled cylinder is related to the pressure (P, atm), radius (r, in.), and wall thickness (t, in.) as follows:[3]

$$P = \frac{St}{14.7r} \tag{3}$$

For S = 30,000 psi, t = 0.375 in. and r = 6.0 in., P = 127 atm or 1875 psi.
Thus, for the illustrative case above, the yield stress in the canister is
approached at about 800°C. When the calcine temperature does not reach 800°C,
the complete decomposition assumed in the above calculations may not take
place. However, loss of cooling could result in a temperature excursion and
in pressurization of the canister, increasing the hazard of corrosion or
rupture. For example, the heat flux in the reference calcine canister is
about 4960 Btu/(hr)(ft^2)(15.64 kW/m^2) at a cooling time of one year. If
water cooling is assumed to be lost and if black body radiation to cool
surroundings is also assumed, the canister wall temperature would be about
850°F (454°C), which is 722°F (401°C) higher than that for water storage.
The resulting waste centerline temperature would be about 1201°C. If the
residual nitrate and water are both reduced to the level of 0.1 wt % before
the canister is sealed, the potential pressure as calculated by equation 1
for several calcine temperatures would be

100°C	4.39 atm
400°C	7.93 atm
800°C	12.64 atm

These pressures result in canister tensile stresses that are less than 10%
of the ambient yield stress and 25% of the 800°C yield stress. Thus, overall
canister reliability would be enhanced if the calcine could be denitrated and
dehydrated to residual levels of 0.1 wt %. Although use of a reductant (*e.g.*,
hydrogen) may be effective at somewhat lower temperatures for this purpose,
only thermal decomposition at temperatures of 800°C or higher are considered
here for reasons of simplicity.

6.2. Stabilizing Waste Calcine for Canister Storage

6.2.1. Background

The major requirements or design criteria applied to packages
of solid waste in retrievable canisters are strength, inertness, and impene-
trability of the package. The above general criteria are intended to cover
the overall aspects of stability and leachability of the package as a whole,
including interactive effects of individual components of the composite waste
package and features of the environment that affect package integrity.

In this section is discussed the inertness or stability of the
solid waste form itself, with respect to its compatibility with the canister.
Leachability (*per se*) of the solid waste form is not considered because the
canister, if it remains intact, is capable of preventing leaching of the
solid waste. Specifically, a possible method of treatment of solid calcined
waste to improve its inertness and stability is discussed.

The corrosion behavior of the metal containment of storage bins
and the mobility of fission products in temperature gradients have been
reported by the Idaho Chemical Processing Plant for calcine containing alu-
minum or zirconium from cladding.[4] At wall temperatures of about 100°C and
bulk calcine temperatures not exceeding 700°C, wall corrosion of stainless
steel type 304 is no more than 1 mil/century (0.25 µm/yr). After the fission
products have been cooled for six years, only cesium and ruthenium undergo

vapor transport at temperatures above 600°C; since these appear to redeposit at temperatues of about 500°C or lower, they appear to offer no special hazard to containment.[5] Although these data on calcine are not considered definitive for all possible forms of commercial wastes that might be encountered at a future RSSF, the present expectation is that with adequate temperature control solid calcine will not be corrosive to type 304 stainless steel while the calcine remains in the unmelted condition.

The major concern with the potential of calcine for exerting a deleterious effect on the stainless steel canister is that pressurization may occur due to decomposition of the residual nitrate (and to a lesser extent, water) in the calcine. As discussed earlier, the potential pressure depends on the amount of nitrate and water present. Decomposition of nitrates can occur either slowly from radiation or rapidly due to elevated temperatures (>800°C).

For calculation of internal pressures, it can be shown that the volumetric average of gas temperatures is the average of the centerline temperature and wall temperature (see Section 8.3.1).

6.2.2. A Method of Decreasing Residual Nitrate and Water in Calcine for Canister Storage

It appears that a 800°C heat treatment of the calcine before sealing of the canister would decompose the residual impurities to levels which no longer have the potential for serious pressurization. This post-treatment of calcine could be done in a special vented vessel before the calcine is charged to the canister, but it also appears possible to heat-treat while the calcine is in the canister (before the canister is sealed).

The suitability of in-canister heat treatment of calcine can be considered in terms of standard practices for the heat treatment of stainless steel 304L. The melting point of stainless steel is about 1400°C. Stress relief (*e.g.*, for welds) is carried out by one- to two-hour treatments at 900 to 1000°C, followed by controlled rapid cooling. In such cooling operations, the temperature range of 790°C to 430°C is critical, because if the steel is held too long in this range of temperature, carbides may precipitate in the grain boundaries, leaving the stainless steel in a sensitized condition for subsequent corrosion. The low carbon content of 304L, however, reduces its susceptibility to sensitization. Precipitated carbides can be redissolved by treatment at about 1120°C, followed by a rapid quench.[6,7] Rapid cooling itself does reintroduce some stresses. If these are excessive, a lower rate of cooling may be employed, but at the additional risk of some sensitization. In practical cases, a balancing of the two effects may be required.

From the above data on decomposition temperatures of calcine and on allowable temperatures for stainless steel, it appears that a heat treatment of the filled and vented canister at about 900°C would have the desirable effect of decomposing residual nitrates in the calcine and of stress-relieving the canister.

The feasibility, in practice, for this method would depend on the behavior of the calcine, *i.e.*, the effectiveness of thermal decomposition

with no melting or sintering, and on a suitable means of supporting the filled canister to prevent distortion. General operations, atmosphere control, and temperature control would have to be carefully checked to verify that no canister corrosion or other damage occurred.

Apparently, heat treatment could be accommodated within the basic design of the reference system. The volume of vent gas is small compared to gas volumes handled in calcination. Fission products volatile at 800°C in the central regions of a canister are substantially condensed on a bed of calcine or alumina at temperaturs below 600°C in the cooler regions. The operations of sealing, welding, and annealing a vent do not differ from those involved in any reference procedure for filling and sealing a canister.

6.3. Migration of Fission Products in Reactor Fuels

The behavior of fission products in reactor fuels may provide some insight into what might occur inside a waste canister. It is recognized that the oxidizing conditions in a fuel element that is in a reactor probably lead to the formation of fission product compounds that are dissimilar to the oxide forms of fission products formed during calcination. In addition, the temperatures in fuel elements are much higher than expected in waste storage.

The fission product receiving the greatest attention is cesium, principally because intergranular attack of the stainless steel cladding wall is attributed to it.[8] Microprobe examinations conducted in the Chemical Engineering Division at Argonne have revealed the presence of cesium molybdate in the reaction layers adjacent to and in the grain boundaries of the stainless steel clad. Further, cesium concentration gradients verify that the cesium has migrated to the clad wall from hot regions of the fuel. Postulated mechanisms of transport include vaporization, migration, and condensation of cesium and/or cesium molybdate.[8,9]

In ANL work, the presence of tellurium in reaction layers has also been observed by microprobe examination. Some experimenters feel that it, too, is a contributor to localized corrosion of the cladding.[8]

At a 1973 conference,[10] several other fission products were identified in reaction layers by investigators. In irradiation experiments conducted in the Dounreay Fast Reactor, "Gross radial migration of the volatile alkali metals towards the fuel/clad interface occurs in almost all oxide fuel pins, and limited axial migration towards the cooler end of the fuel column is regularly observed."[11] In Rapsodie, ^{137}Cs, ^{131}I, and ^{132}Te were found to migrate toward the clad, and ^{103}Ru and ^{106}Ru toward the center.[12] In another French experiment conducted at high burnup, cesium, molybdenum, palladium, barium, and tellurium were identified in the several layers near the clad, while barium and tellurium were also found in the grain boundaries of the clad.[13]

The oxides of the rare earths and zirconium are quite stable, have low vapor pressures, and are not expected to migrate significantly.

The above information on oxide reactor fuels is indicative that fission products other than cesium are candidates for migration in an oxide waste canister. The lower temperatures present in a canister are likely to arrest or prevent migration, but this needs to be examined.

6.4. Effect of Solid Waste Form on Interior Wall of Canister

As discussed in Section 4, the properties of the dry solid waste--either calcine or glass--are such that, when the temperature at the canister wall is below the liquidus temperature, there is no evident basis of chemical attack of the canister wall. This is true for the reference stainless steel and for any other metal that has a protective oxide film to air at this temperature.

Other factors relevant to the effect of the contained waste and possible canister attack are (1) gas pressures (from calcine impurities) and (2) solid pressures (expansion effects of either calcine or glass). These are discussed elsewhere in Sections 3, 4, and 8. There appears to be no decomposition or segregation effects of either the reference calcine or the reference glass that could result in an aggressive chemical species concentrating at the inside canister wall. One conceivable effect of this sort in the case of calcine would be a result of transport and concentration of caustic from residual water. It is expected that the water content of the waste would be reduced to levels which remove the possibility of this avenue of attack.

There is a general lack of information about interactions between the glass waste form and stainless steel in the temperature range of interest. Though it is likely that interaction effects are low or nonexistent, it would be prudent to conduct experiments to ensure that no problems exist.

References for Section 6

1. Retrievable Surface Storage Facility Alternative Concepts Engineering
    Studies, AEC Report ARH-2888, Rev., pp. 11-14 (July 1974).

2. Environmental Statement, Calcined Solids Storage Additions, National
    Reactor Testing Station, Idaho, USAEC Report WASH-1529, p. 5 (April 1973).

3. T. Baumeister (Ed.), Standard Handbook for Mechanical Engineers, 7th
    Edition, p. 5-64, McGraw-Hill Book Company, New York (1967).

4. T. L. Hoffman, Corrosion Monitoring of Storage Bins for Radioactive
    Calcine, presented at 1975 Conference of NACE, April 14-18, 1975, to
    be published (same author and title) as ICP-7071 (May 1975).

5. M. W. Wilding and D. W. Rhodes, Stability Studies of Highly Radioactive
    Alumina Calcine During High Temperature Storage, IDO-14670 (January 1966).

6. J. L. Everhart, Engineering Properties of Nickel and Nickel Alloys, Plenum
    Press (1971).

7. T. Lyman (Ed), Metals Handbook, 8th ed., Vol. 2, American Society for
    Metals, Novelty, Ohio (1964).

8. M. G. Chasanov et al., Chemical Engineering Division, Fuels and Materials
    Chemistry Semi-Annual Report, January, 1973 to June, 1973, ANL-8022,
    pp. 31-41 (December 1973).

9. C. E. Johnson et al., Chemical Engineering Division, Fuels and Materials
    Chemistry Annual Report, July, 1973 to June, 1974, ANL-8122, pp. 37-39
    (January 1975).

10. Proceedings of a Symposium on Fuel and Fuel Elements for Fast Reactors,
    Vol. 1, Brussels, July 2 to 6, 1973, International Atomic Energy Agency,
    Vienna (1974).

11. K. G. Bagley et al, Fuel Element Behavior Under Irradiation in DFR,
    Ref. 10, pp. 87 to 100.

12. J. L. Ratier, C. Mercier, and F. Anselin, Comportement des Elements
    Combustibles du Reactor Rapsodie Durant Les Annees 1971 et 1972,
    Ref. 10, pp. 101 to 109.

13. M. Conte et al., Examen des Reactions Entre Oxyde et Gaine dans L'Experience
    G5 a Fort Taux de Combustion, Ref. 10, pp. 197 to 220.

7. CONDITIONS AND METHODS OF CONTROL OF EXTERNAL ATTACK

7.1. Review of Localized Corrosion Behavior of Stainless Steel in Water Environments

7.1.1. General

An effort has been made to identify the behavior of austenitic stainless steels--with emphasis on types 304 and 304L--when exposed to environments and conditions comparable to those expected in the storage of solidified high-level waste in a Retrievable Surface Storage Facility (RSSF).

In general, austenitic stainless steels of the 18-8 type (18% chromium and 8% nickel) have excellent surface corrosion properties in both water and aggressive oxidizing environments. However, under some conditions, these steels are also subject to severe localized attack that leads to early failure. The reliability of the use of austenitic stainless steels as canister materials is determined by the potential of such localized attack.

The following forms of localized attack have been identified:

a. Stress corrosion cracking
b. Intergranular attack
c. Pitting

It is necessary to ascertain, as well as possible, the envelope of conditions within which a significant potential exists for local corrosion phenomena, to determine whether the reference conditions of storage in the RSSF infringe on that envelope, and, if so, to determine the reliability of the canister.

Localized attack phenomena are strongly dependent on the thermal history of austenitic stainless steels. In normal use for corrosive service, these steels are heat-treated at temperatures (usually greater than 1000°C or 1830°F) at which their constituents are solubilized. The solid solution austenitic phase thus formed is forcefully retained by rapid cooling. The nonequilibrium alloy is subject to changes when it is exposed to temperatures where atom mobility is increased. These changes, in turn, may have an effect on local corrosion behavior.

Carbon is almost always present as an impurity in austenitic stainless steels, and special efforts are usually made to keep its content low in order to reduce known adverse effects. For example, the specification for carbon content of type 304 stainless steel is a maximum of 0.08% and the specification for type 304L is a maximum of 0.03%. Although reliable data for carbon solubility as a function of temperature is lacking, some general observations can be made. Carbon solubility decreases markedly with decreasing temperatures, and it is known that at temperatures of 550 to 850°C (1020-1560°F), the solubility is greatly exceeded in normal grades of stainless steel (*e.g.*, type 304) and is even exceeded in the low-carbon grades (*e.g.*, type 304L). It is generally agreed that carbon tends to form a precipitate with the chromium contained in the alloy ($Cr_{23}C_6$) and that it does so preferentially along grain boundaries. Such alloys are said to be sensitized. Sensitization is significant because it adversely affects the corrosion-resistance of stainless steels in many environments and frequently contributes to accelerated local attack.

7.1.2. Stress Corrosion Cracking

Emphasis in this review is on stress corrosion cracking of stainless steels in water environments. The severity of this phenomenon is dependent on many factors, including temperature, stress level, dissolved oxygen and chloride concentrations in the water, and the state (sensitized or unsensitized) of the stainless steel.

It was anticipated that a review would allow definition of the upper limits of the various parameters, below which it can be assumed with high probability that stress cracking does not occur. This objective may be somewhat elusive, as illustrated by a statement by Latanision and Staehle in a paper presented at the 1967 conference on the Fundamental Aspects of Stress Corrosion Cracking: ". . . there is great difficulty in defining a minimum chloride concentration below which cracking will not occur because of effects of the concentrating processes such as drying or boiling."[1]

A great deal of work has been done in water environments at temperatures characteristic of those in light water reactors, *i.e.*, 200 to 300°C (390-570°F). Far less work has been done at the lower temperatures of interest for the RSSF, namely, 60 to 90°C (140-190°F), although some efforts have been made to determine the effect of temperature on cracking behavior. Included below is a review of published information at a number of temperatures. Although data in the temperature range of 150 to 300°C is not directly applicable, it does provide a basis for analyzing trends and sensitivities.

At 200°C (390°F), stress cracking of type 304 stainless steel has been observed in water environments with chloride concentrations as low as 2 ppm in the essential absence of oxygen (0.78 ppm).[2] The specimens tested were fully annealed, 0.015-in.-dia wires, and were stressed at a level of 90% of the yield stress (*i.e.*, at about 32,000 psi). Failure times ranged from 480 to 938 min. At higher concentrations of chloride (100 ppm NaCl) and oxygen (10 to 15 ppm), time to cracking was reduced to about 50 min for all stress levels tested between 60 and 100% of the yield stress (21,000 to 35,000 psi), and to 300 min for 40% of the yield stress (14,000 psi). No tests at lower stress levels were conducted, although these might have allowed a threshold stress to be determined. Increasing the temperature to 260°C also resulted in short cracking times (∿70 min) at 100% of yield, but cracking tendencies were reduced considerably with reduction in stress. The data suggest that the threshold stress is higher at 260°C (500°F) than at 200°C (390°F).[3] The results also suggest that microstresses rather than gross loading stresses are determinative of stress cracking (see Section 7.1.4.5. below).

Figure 7.1. shows a compilation of data relating chloride and oxygen concentrations to cracking time.[1,4] The data is for type 304 stainless steel stressed at a level of 21,000 psi (∿60 per cent of the yield stress) at 260°C (500°F). When sodium chloride concentrations are high--about 2000 ppm--cracking times are nearly independent of oxygen concentration, but at low concentration, the oxygen concentration has a much more pronounced effect on stress cracking.

Although these types of tests with wire specimens are severe because the specimens have a high surface to volume ratio, they nonetheless

are indicative of conditions that favor adverse behavior. Specimens consisting of thick sections of metal do not fail as rapidly as thin wires do.
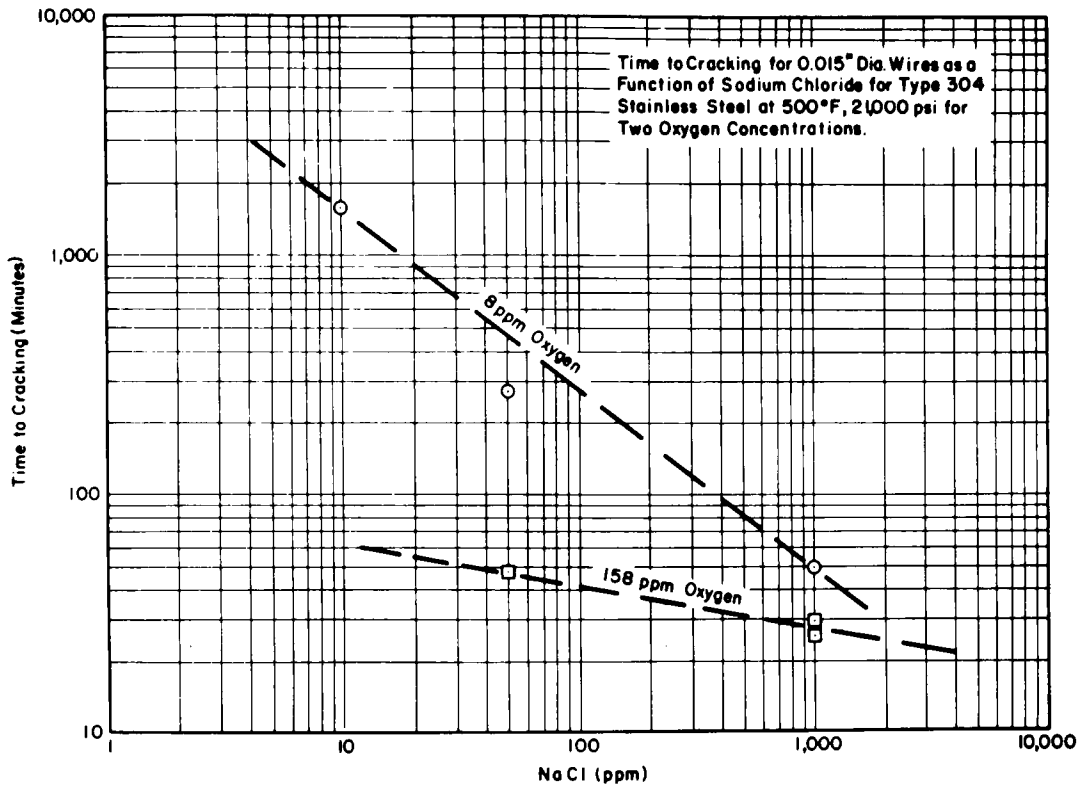
Fig. 7.1. Effect of Chloride and Oxygen Concentrations on Time-to-Cracking of Type 304 Wire Held at Constant Load in Single-Phase Aqueous Environment[1]

Sensitized stainless steel is more prone to stress cracking than is annealed material. The mode of cracking is transgranular in annealed material and intergranular in sensitized steel. Further, in sensitized material, the presence of chloride ions is not a prerequisite to initiate cracking; the presence of oxygen alone is sufficient.

Sensitized specimens in the forms of plates and internally pressurized cylinders at a temperature of 288°C were exposed to water containing various amounts of oxygen and no chloride at three different stress levels.[5] The alloys used were types 304 and 316 stainless steel, and the stress levels were about 27,000, 54,000, and 81,000 psi (yield stress is about 32,000 psi at 288°C (545°F). No failures were observed in periods ranging up to 450 days when oxygen levels were held at 10 ppm or less and stresses were 54,000 psi or less. At the highest stress level (81,000 psi) and oxygen concentration of 10 ppm, failure was observed at 14 days for type 304 stainless steel and at 10 days for type 316. At oxygen concentrations of 100 ppm, type 304 stainless steel failed rapidly at all stress levels (mill-annealed material does not fail under these conditions).

Other investigators have found that at stress levels above yield, an increase of oxygen level from 0.2 to 5 ppm (also at 288°C or 545°F) results in sensitized type 304 stainless steel changing from a non-cracking region to a cracking region.[6]

Figures 7.2 and 7.3 show the pronounced effects of dissolved oxygen level and stress level on the time to cracking for sensitized type 304 stainless steel.
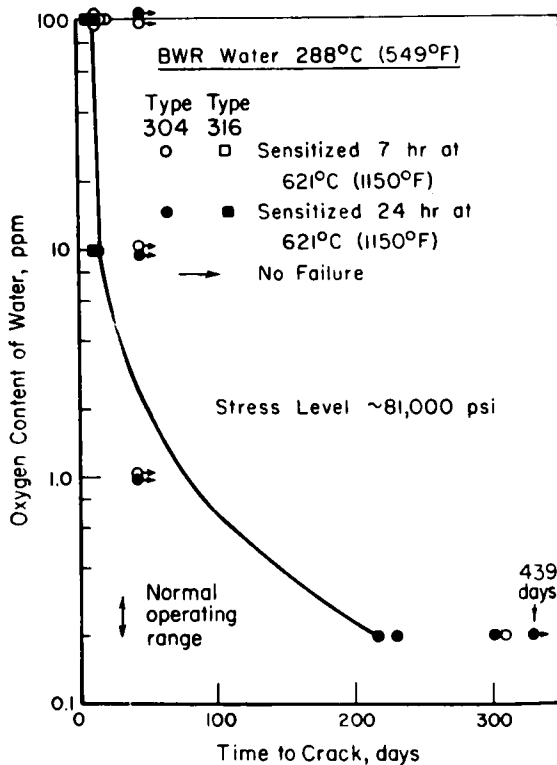
Fig. 7.2.

Effect of Dissolved Oxygen Level on Time-to-Cracking of Stressed Sensitized Stainless Steel Specimens in Water at 288°C (545°F).[5]

Fig. 7.3.

Effect of Stress Level on Time-to-Cracking of Sensitized Types 304 and 316 Stainless Steel in Water.[5] (To convert psi to N/m^2, multiply by 6.895 x 10^3.)
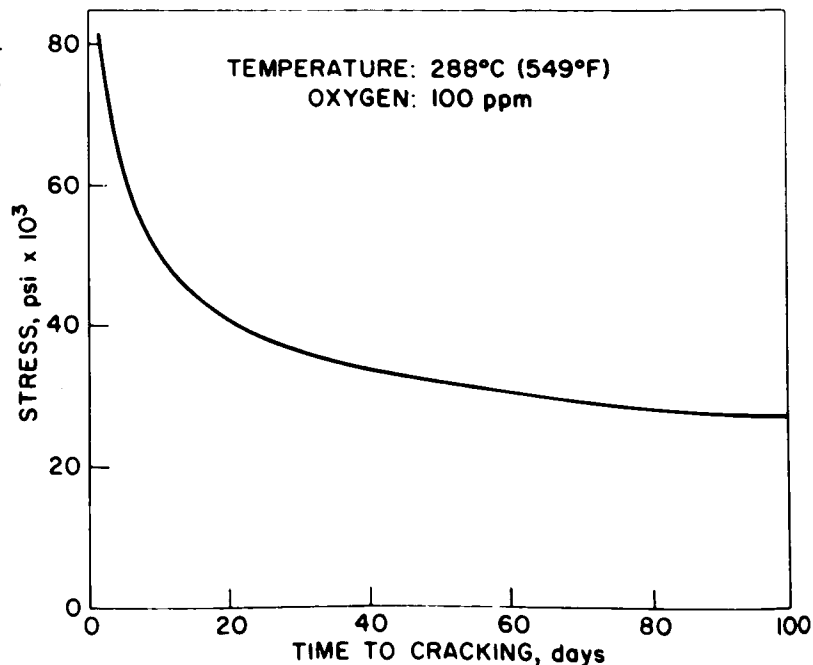
Stress corrosion cracking can also be induced in annealed types 304 and 347 stainless steels when they are exposed to chloride-containing water in a temperature range of 60 to 90°C (140-190°F). Highly stressed U-bend specimens were exposed to water containing 5 to 550 ppm sodium chloride in equilibrium with ambient air.[7] Oxygen concentrations ranged from 2.75 ppm at the lower temperature to 0.88 ppm at the upper temperature. During test periods of 48 hr in water containing 10 ppm sodium chloride, 10 percent of annealed type 304 specimens cracked at 60°C (140°F), while 90 percent cracked at 85°C (185°F). When specimens were sensitized, comparable cracking figures were 60 and 100 percent. In one series of tests in which oxygen was bubbled through the water, cracking failure rates did not increase significantly.

The above data establish that stress cracking can occur in type 304 stainless steel at the temperatures of interest for underwater storage at the reprocessing plant and the RSSF (water basin concept), even under conditions in which no mechanisms are available for local concentration of chloride. It is recognized that these tests were conducted only at high stress levels well beyond the yield stress, and that they shed little light on the effect of various stress levels below yield stress on cracking tendencies or on the existence of a threshold stress level below which cracking does occur.

A summary of data from a variety of sources relating cracking time to temperature of exposure is shown in Fig. 7.4.[8] Included is data obtained for a number of stainless steels generally regarded as the 18-8 type in solutions containing 25 ppm or more of chloride. Stress levels are not stated but in general are those associated with U-bend tensile specimens stressed beyond the yield stress. The pronounced effect of temperature is evident. The figure does not substantiate the very low temperature sensitivity to stress corrosion cracking identified in Reference 7.

Several efforts have been made to establish threshold conditions for the initiation of cracking. Figure 7.5 relates suggested oxygen and chloride threshold levels for annealed type 347 stainless steel exposed to water at 260°C (500°F).[9] The authors pooled all data available to them, neglected all parameters except oxygen and chloride, and considered only whether specimens had failed or not.

Results of one of the few efforts to establish threshold stresses for annealed stainless steels are shown in Fig. 7.6.[1,10] The figure was constructed from data obtained using boiling solutions of concentrate magnesium chloride (42%) and indicates a threshold stress of about 10,000 psi. Although this environment is regarded as being highly agressive, it is recognized that effects associated with it are sometimes different from those obtained with other chloride salts. More data on threshold stresses are needed to more fully evaluate the behavior of type 304 stainless steel at the conditions of interest.

Most of the studies on stress corrosion cracking provide values of parameters that ensure that cracking will occur in water environments. Stresses above the yield stress, temperatures about 175°C (345°F), and chloride and oxygen levels above 5 ppm are highly conducive to promoting cracking. Extrapolation of existing data strongly suggests that at low stress levels and low temperature, cracking can be avoided. Data supporting this observation are generally lacking, however.
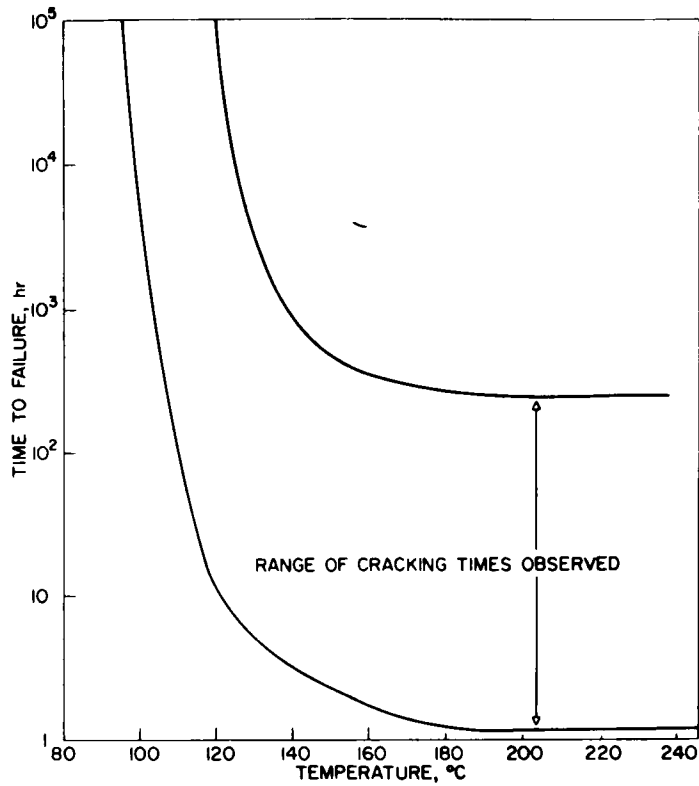
Fig. 7.4. Influence of Temperature on Time-to-Failure
for Highly Stressed 18-8 Stainless Steel in
Solutions Containing >25 ppm Chloride.[8]
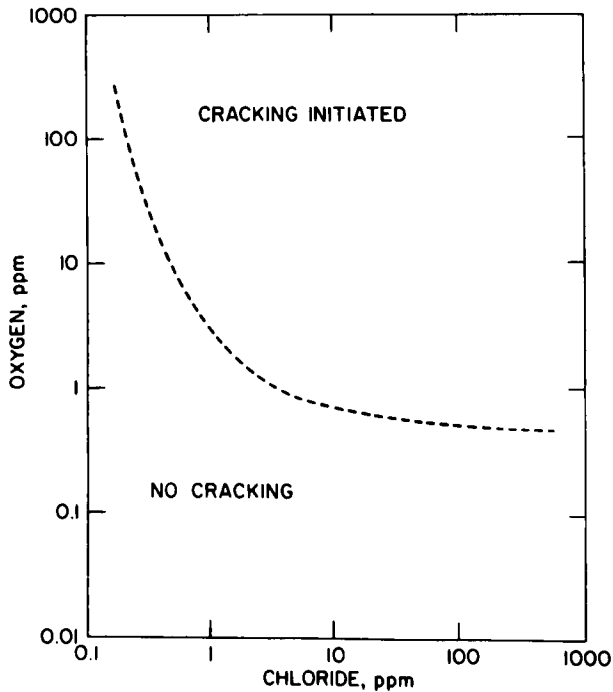
Fig. 7.5.

Proposed Threshold Levels for Cracking
Related to Oxygen and Chloride Content
of Water at 500°F (260°C) Applied to
Type 347 Stainless Steel at High Stress
Levels.[9]
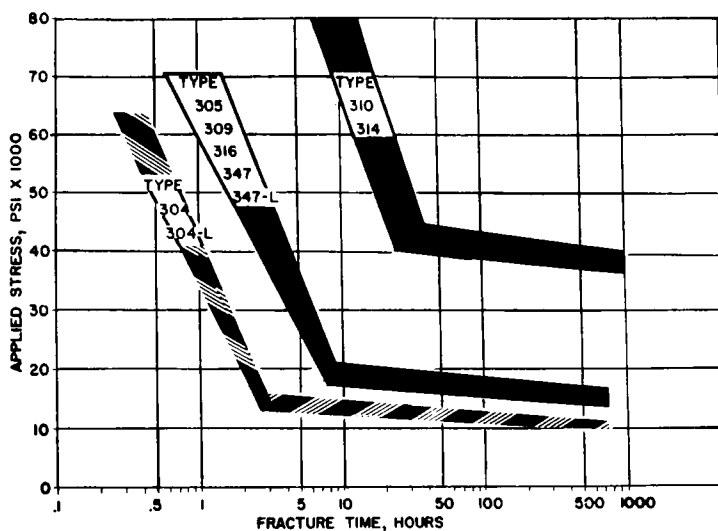
Fig. 7.6.   Composite Curves Illustrating the
Relative Stress Corrosion Cracking
Resistance for Commercial Stainless
Steels in Boiling 42% Magnesium
Chloride (309°F or 155°C).[1,10]

In the following sections, several sources of stress in waste
canisters are identified. Calculations of the magnitude of developed stresses
are presented.

7.1.3.   Temperature-Induced Stress in Stainless Steel Canisters Containing Solid Glass

In order to minimize the potential failure of waste canisters
in a water environment, the stress in stainless steel canisters must be
restricted to low levels. No design threshold stress level has been established,
but a reasonable strategy is to hold the stresses as low as practicable.

A calculational model for canister stresses has been developed
along standard methods.[11] The reference case is borosilicate glass cast
directly into a canister of type 304L stainless steel having an ID of 12.0 in.
and a wall thickness of 0.375 in. The glass assumes a rigid solid form at a
temperature well above the storage temperature of the canister. Because the
thermal contraction of stainless steel is greater than that for glass, cooling
the canister results in the development of circumferential tensile stresses
in the canister.

Stresses calculated by use of a simple model have been compared
with stress levels known to be conducive to the initiation of stress-corrosion
cracking in oxygenated water that contains chlorides. The mechanical properties
of type 304 stainless steel and Pyrex (commercial grade borosilicate glass) were
used, and the model was developed so that the effect of variables is evident by
parameteric analysis. The model assumes that the materials are only subject to
strains within the elastic limit and that no "creep" phenomena are involved.

The stresses in the stainless steel canister can be treated as those in a thin-wall cylinder, where the tensile stress is closely approximated by the following:

$$S_s = E_s\left(\frac{\Delta r_s}{r}\right) = \frac{p_s r}{t} \qquad (1)$$

where

S_s = circumferential tensile stress, psi

E_s = modulus of elasticity of stainless steel, psi

r = inside radius of canister, in.

Δr_s = absolute deformation (increase) in radius of steel within the elastic limit, in.

$\dfrac{\Delta r_s}{r}$ = relative elastic deformation, or strain

t = thickness of canister wall, in.

p_s = radial pressure acting on the inside wall of the canister, psi

For the solid cylinder under external pressure, the deformation is given by the following:

$$\frac{\Delta r_g}{r} = \frac{p_g\left(1 - \mu_g\right)}{E_g} \qquad (2)$$

where

p_g = the external (radial) pressure applied, psi

r = inside radius of canister (same as r above), in.
  = radius of the glass

Δr_g = absolute deformation (decrease in radius) of glass, in.

E_g = modulus of elasticity for Pyrex, psi

μ_g = Poisson's ratio for Pyrex

At some high temperature below which glass is considered rigid, it is assumed that the internal diameter of the canister and the external diameter of the glass cylinder are identical and that no stresses exist in either material. The decreases in diameter with cooling, assuming no restraint, are, for stainless steel:

$$2r \cdot c_s \cdot \Delta T \qquad (3)$$

and for glass:

$$2r \cdot c_g \cdot \Delta T \tag{4}$$

where
c_s = coefficient of thermal expansion of steel canister, $°F^{-1}$

c_g = coefficient of thermal expansion of the glass cylinder, $°F^{-1}$

ΔT = temperature decrease from initial high temperature at which glass is considered rigid, $°F$

Consolidating the above information and using the proper sign to show increase or decrease in radii, one obtains

Change in radius of glass:

due to cooling (from Eq. 4): $-rc_g\Delta T$

due to external stress (from Eq. 2): $-\dfrac{p_g\left(1 - \mu_g\right)r}{E_g}$

Change in radius of stainless steel:

due to cooling (from Eq. 3): $-rc_s\Delta T$

due to elastic strain (from Eq. 1): $+\dfrac{p_s r^2}{tE_s}$

In the final stressed condition, the algebraic sum of the changes in radius of stainless steel must equal the sum of the changes in radius of the glass

$$\frac{p_s r^2}{tE_s} - rc_s\Delta T = -rc_g\Delta T - \frac{p_g\left(1 - \mu_g\right)r}{E_g} \tag{5}$$

Further, the external stress on the glass (p_g) is equal to the inwardly directed stress due to elastic strain of the stainless steel (p_s), which in turn is equal to $S_s t/r$ from Eq. 1. Substituting $S_s t/r$ and multiplying by E_s/r, one obtains

$$S_s - E_s c_s\Delta t = -S_s \frac{t}{r}\frac{E_s}{E_g}\left(1 - \mu_g\right) - E_s c_g\Delta T \tag{6}$$

which yields

$$S_s = \frac{E_s \Delta T \left(c_s - c_g \right)}{1 + \frac{t}{r} \frac{E_s}{E_g} \left(1 - \mu_g \right)} \tag{7}$$

For the properties in Table 5.1 and for a cylinder diameter of 1.0 ft, the stress S_s in psi is given by

$$S_s = 214 \, \Delta T \tag{8}$$

This indicates that a tensile stress of 21,400 psi develops in the steel for every 100°F of cooling. Since the softening point of Pyrex is about 1500°F (815°C) and the reference temperature of the canister in water-basin storage is about 140°F (60°C), the ΔT may be 1000°F (540°C) or higher.

These calculations (which neglect stress-relieving mechanisms such as creep) show that on cooling, large circumferential tensile stresses in the stainless steel canister may develop that may lead to stress corrosion cracking, deformation, or rupture. The phenomenon of stress relief (discussed below) is important in relation to the reliability of canisters during interim storage of high-level wastes.

7.1.4. Methods of Stress Relief

Stresses imposed by cooling could be removed by creep strain (*i.e.*, essentially instantaneous plastic deformation at high stress), or shot peening.

Also germane to stress relief is consideration of (1) the thermal expansion coefficients of various glasses in comparison with the value used in the preceding section, and (2) the viscosity of glasses in a stress-relieving mechanism.

7.1.4.1. Stress Relief by Creep

Creep rates for both stainless steel and glass are highly temperature dependent. At temperatures below about 750°F (400°C), creep rates of steel and glass are so low that this method is not practical to effect major stress relief. Therefore, since creep is not effective for stress relief for the final cooling in the range of 750 to 150°F, very large residual stresses, well in excess of the yield stress, would remain.

7.1.4.2. Stress Relief by Yield

As the filled canister is cooled to 750°F and lower, stresses in the stainless steel will rapidly increase to and exceed the yield stress (about 39,000 psi), at which point yield strain will occur and stress will no longer increase as calculated for elastic strain.

However, the magnitude of stress required to reach the yield point increases in 304L steel with continuing deformation; this phenomenon is termed <u>work hardening</u>. The extent of work hardening is related to the total amount of plastic deformation or strain. The maximum possible strain of stainless steel required for this application is associated with differential thermal contraction during cooling--about 1.5%. This amount of deformation is well below the elongation for rupture which, for fully annealed metal, is more than 50% and for cold-worked metal is 9% or more. If the strain is 1.5%, the yield stress will not rise above about 40,000 psi.

7.1.4.3. A Subcooling Method of Stress Relief

The elastic tensile load stress that remains in the canister after the solidifed glass is cooled can be removed by continuing the cooling below the reference waste storage temperature ($\sim$140°F). The additional cooling will cause the stainless steel to yield further. If this additional yield strain is as large as the elastic strain at the yield stress, then when the temperature is increased to the storage temperature, the elastic load stress will be completely removed. Thus this source of stress will not be present to produce stress-corrosion cracking in subsequent exposure of the canister to the storage environment. The operations involved in subcooling are shown in Fig. 7.7.
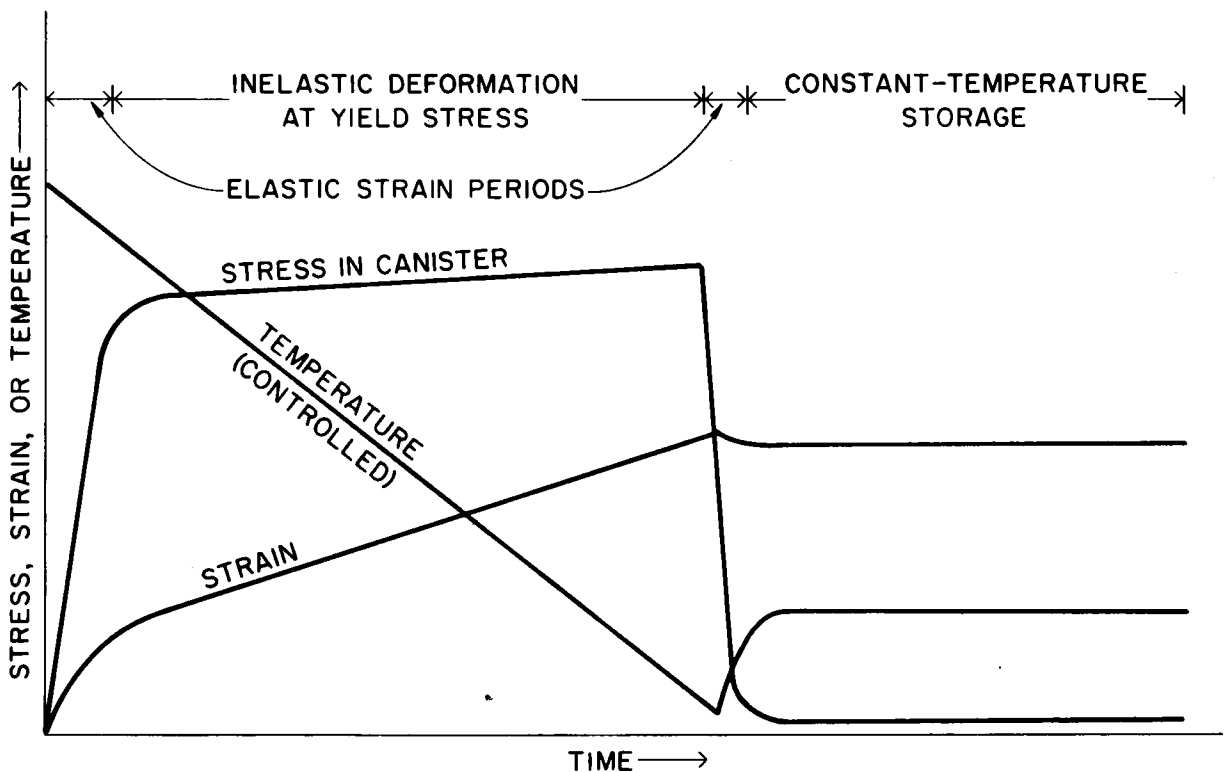
Fig. 7.7. Stress-Strain History for Controlled Cooling of
           Glass-Containing Canister to Achieve Near-Zero
           Final Load Stress

The amount of subcooling below 140°F required to effect complete stress removal depends on the properties of the materials, and the storage temperature, T_s, as follows:

$$\left(T_s - T_{sc}\right)(\Delta C) = \frac{S_y}{E_s}$$

or

$$T_{sc} = T_s - \frac{S_y}{E_s(\Delta C)}$$

where

T_s = storage temperature, °F

T_{sc} = minimum cooling temperature, °F

ΔC = differential thermal expansion, for SS304 and Pyrex, approximately $8.6 \times 10^{-6}/°F$

S_y = yield stress in stainless steel at T_{sc}, including the effect of work hardening, approximately 40,000 psi

E_s = modulus of elasticity in stainless steel T_{sc}, approximately 29×10^6 psi

For the values indicated,

$$T_s - T_{sc} = \frac{40,000}{(29 \times 10^6)(8.6 \times 10^{-6})}$$

$$= 160°F$$

If

$$T_s = 140°F$$

then

$$T_{sc} = -20°F(-29°C)$$

The reduction of circumferential tensile stress to zero by this method will require close control and accurate knowledge of the properties used above. Stainless steel 304L has generally good properties at subzero temperatures. The tensile strength increases markedly at low temperature and this will affect the stress-strain relationship.

The practical utility of the subcooling method of removing elastic load stress is, however, limited, since (1) it involves special low-temperature cooling, which has practical difficulties, (2) it

results in additional deformation which may damage the canister, and (3) it
does not remove the residual internal stresses in the steel nor does it "heal"
surface defects as does stress relief by high-temperature treatment.

7.1.4.4. A Mechanical Method of Stress Relief: Shot Peening

Since surface tensile stress is determinative of
stress-corrosion cracking, any mechanical treatment of the surface which
tends to apply compressive stresses (or to reduce tensile stresses) will
have a favorable effect in reducing susceptibility to cracking. One of
the most important commercial methods for removing residual surface stresses
is shot-peening, a process in which steel shot at high velocity is propelled
against the surface by a jet of compressed air.[12] The effect of shot-peening
on stress distribution is illustrated in Fig. 7.8. The change of stresses
at the surface from tensile to compressive is evident.
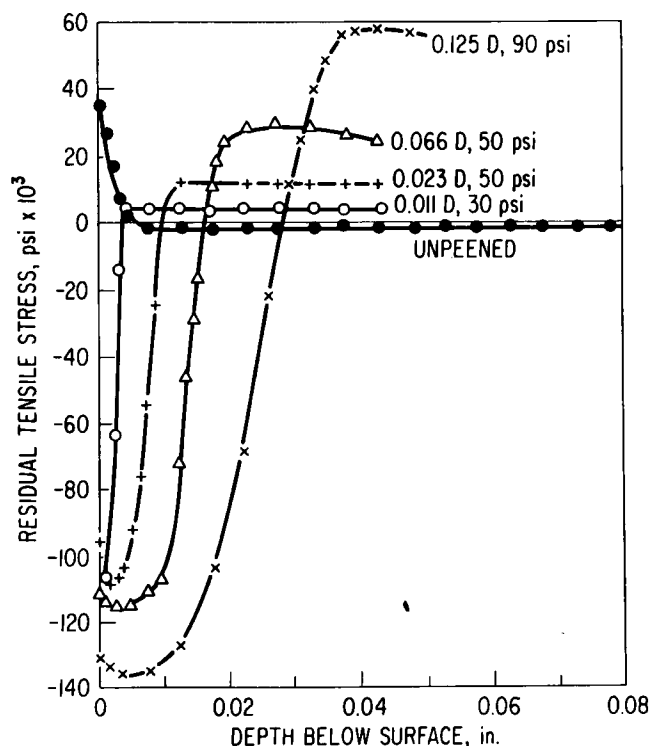
Fig. 7.8. Effect of Shot-Peening.[12] Effect of shot diameter
and air pressure on stress distribution for steel
of hardness $R_C 42$. (Lessells and Broderick, 1956.
Courtesy of Institution of Mechanical Engineers.)
Positive stress is tensile; negative stress is
compressive.

7.1.4.5. Residual Stresses

"Residual stresses" are defined as stresses remaining
in a material in the absence of external loads or changes in temperature, and

they range from microscopic stresses (from misfitting solute atoms and individual dislocations of the crystal lattice) to macroscopic stresses over parts of a material which have undergone uneven plastic deformation (as in bending and welding). Microscopic stresses on a scale somewhat greater than atomic are involved in dislocation pile-ups and other diffusionless shear transformations accompanying plastic strain. Residual stresses play fundamental roles in the initiation and propagation of cracks in stress-corrosion cracking, fatigue failures, and brittle fracture.[12]

The effects of localized residual stresses are the same as the effects of load stress or any other stress. In the absence of load stresses, residual stresses can be removed by relatively little plastic flow. Therefore, relief of residual stress is commonly achieved by increasing the temperature to allow creep strain to take place and offset the elastic strain which gives rise to the residual stress.[12]

The subcooling method of stress relief (Section 7.1.4.3) is capable of removing the bulk load stresses induced in a canister, but residual stresses will probably remain. A heat treatment for removal of the residual stresses would be effective if (1) the adhesion of the glass to the canister is so low that an air gap develops as a result of the differential coefficients of expansion and (2) the glass does not flow to fill the gap, re-creating the conditions that produced the bulk load stress initially. If these two conditions cannot be met, alternative methods of relieving residual stresses would be required.

7.1.5. Alternative Methods for Reducing Susceptibility of a Stainless Steel Canister to Stress-Corrosion Cracking

If methods of stress relief such as those discussed above are not effective for canisters containing waste, and if stress-corrosion cracking (SCC) proves to be a serious problem in canister storage, alternatives in the operational design for high-level waste handling could be used, for example:

a. precasting of glass and "cold" insertion of the casting into the canister,

b. use of an internal, stress-absorbing liner for the canister,

c. use of an outer, secondary container for contact with water,

d. use of air cooling rather than water cooling for storage and shipping,

e. use of a surface coating that is immune to stress-corrosion cracking,

f. use of an alloy other than stainless steel type 304L for the canister, an alloy that is relatively more immune to SCC.

Since the surface of the canister is of prime importance in SCC, a method of surface treatment that would reduce susceptibility to SCC would be desirable. One such treatment is that reported in a review article

by Latanision and Staehle.[13] A diffused nickel surface on 18-8 stainless steel was found by some investigators to be the surface treatment that conferred the greatest resistance to cracking. A layer of nickel about 0.12 mm thick was deposited by electroplating; then, this layer was diffused by heating to 1010°C for 100 hr.[13]

The above change of the surface alloy composition by depositing a layer of nickel is consistent with a compilation of the cracking susceptibilities of alloy steels as a function of nickel composition. In the words of the report, "The ferritic stainless steels (*e.g.*, type 430) with no nickel do not crack, nor does Inconel 600."[13] It would appear that SS304, which contains 8% nickel, is the most vulnerable composition from this particular standpoint.

However, all alloys (including type 430 stainless steel) and surface treatments have some damage susceptibility; careful evaluation for the full range of conditions would be required before designers consider them for the reference canister and RSSF.

7.1.6. Corrosion of Stainless Steel in Air

The austenitic 18-8 Cr-Ni steels, including 304L, are all resistant to ambient atmospheric conditions, including wide variations of humidity. In long-term tests, these steels remained substantially unaffected.[14]

The oxidation resistance of 18-8 stainless steels at elevated temperatures is high, at least up to 800°C. At temperatures of 600°C in air, low corrosion rates are reported.[15]

Although RSSF conditions include 100-yr time periods, well beyond the duration of any recorded tests, the generally good behavior of 18-8 stainless steel at elevated temperatures and the fact that heat dissipation and temperature decline significantly with time in storage seem to indicate that the reference alloy is highly qualified.

It is possible for higher temperatures to occur during filling of the canister or even during shipping. But short-term oxidation effects at temperatures up to 1000°C are expected to be minor. Of possibly more importance is exposure to temperatures in the sensitizing range of 800 to 1450°F (427 to 790°C).

Thus, temperature control is important from the standpoint of overall resistance of the stainless steel canister to air at elevated temperature. The general corrosion resistance of stainless steel to air at the reference temperatures is extremely high, although some qualification must be made for long-time exposures near the sensitization temperature, 430°C.

7.2. Mechanical Impact and Canister Reliability

As noted in Section 5, the strength and ductility of stainless steel is such that a canister made of schedule 40 pipe is inherently resistant to deformation and rupture by a wide class of mechanical impacts. Mechanical

operations of storage and handling of waste canisters would not normally endanger the canister integrity, nor would accidental dropping of a shipping cask, containing a canister, from modest heights (*e.g.*, 30 ft). This is ensured mainly by the design of the facilities and components and also by establishment of standard operating procedures, as discussed in Section 3 (Reference Description) and Section 8 (Systems Design Considerations).

Extremely high impacts that would be associated with catastrophic accidents must be considered also. The probability of such occurrences can be kept low by facility design. Also, design can prevent extreme impacts and canister rupture that result in dispersion of radio-activity to the environment. This can be accomplished more readily for operations in stationary facilities located in restricted access areas than for conditions associated with shipments.

For the shipping of waste canisters, a wide range of similar but less well controlled accidental impacts must be considered.

7.3. Shipping and Canister Reliability

A large body of design and accident analyses of containers for the shipment of radioactive wastes has been developed. In a study by Sandia Laboratories,[16] a fundamental approach was taken to the consequences of mechanical impacts of various magnitudes in transportation environments. When this study becomes available, its methodology and conclusions should prove useful in quantitative evaluation of waste canister reliability for accidents in general, and for shipment in particular.

In the shipment of solid high-level radioactive waste, the heat dissipation and radiation shielding requirements are of the same sort as for the shipping of spent reactor fuels. Practical limitations of heat dissipation are similar for both types of material, but waste shipments make less severe demands because of several factors:

a. Fission products in wastes are generally of a greater age; certain biologically potent and volatile fission product elements of short half life will have decayed.

b. Certain other volatile fission products, *e.g.*, the noble gases and tritium, will have been eliminated by waste processing.

c. No fissile materials are present, and thus criticality considerations are not relevant.

d. The waste has no intrinsic monetary value.

The principles of design of shielded shipping cases (with cooling means) that conform to performance specifications, safety criteria, and other regu-lations have been summarized by Oak Ridge National Laboratory.[17] The references to internal heat transfer are notable:

"Present regulations do not place a limit on the maximum temperature of a spent fuel element during transport. What they do require is that, under normal conditions of transport, no radioactive material be released from the

containment vessel. Under the hypothetical accident conditions, some activity release, up to specified limits, may be tolerated . . . Regulations do not require a loss-of-coolant assumption; however . . . the assumption will have to be justified in the accident analysis of the cask . . . it is prudent to keep fuel element temperatures as low as possible and, if coolant is lost, below temperatures causing cladding failure."[18] These statements can be made applicable to waste transport, with "solid waste" substituted for "fuel element" and "canister" for "cladding." In general, solid wastes offer less stringent design problems for shipping than do spent fuels, and an optimization of waste cooling time, waste-canister form, and cask cooling method (with contingencies) is likely to differ from that for spent fuel.

Another radioactive shipping study has been made for plutonium fuel material by Pacific Northwest Laboratories.[19] This risk study makes use of Sandia accident analyses cited above. For the case of shipping plutonium dioxide powder, the reference container is a stainless steel pipe, quite similar to the generic reference canister for waste shipment. The dispersion and risks due to accidents were found to be low. The dispersion potential and health hazard of solid waste should be somewhat less than for plutonium oxide, considering that (1) fission products have lower toxicity per gram, (2) the waste shipping cask has heavy shielding in addition to canister containment, and (3) the solid waste is no more dispersible than PuO_2 in the calcine form and is substantially less dispersible if sintered or vitrified, especially in a monolithic glass form.

From the above considerations on shipping, it appears that the base technology of shipping radioactive waste is presently favorable to the shipping of solid high-level waste. Clearly, an extended cooling time (of the order of 10 yr) is favorable to optimizing the reliability of canisters for shipping wastes. If early shipment is required, canister dimensions can be reduced so that the temperature limitations of the waste form and the canister can be met.

References for Section 7

1. R. M. Latanision and R. W. Staehle, Stress Corrosion Cracking of Iron-Nickel-Chromium Alloys, Proceedings of Conference, Fundamental Aspects of Stress Corrosion Cracking, The Ohio State University, Columbus, Ohio, pp. 214-300 (September 11-15, 1967).

2. J. E. Slater and R. W. Staehle, A Study of the Mechanisms of Stress Corrosion Cracking in the Iron-Nickel-Chromium Alloy System in Chloride Environments, April 1, 1970 to June 30, 1970, AEC Report COO-2069-7, Ohio State University Research Foundation.

3. J. E. Slater and R. W. Staehle, A Study of the Mechanisms of Stress Corrosion Cracking in the Iron-Nickel-Chromium Alloy System in Chloride Environments, AEC Report COO-2069-16, Ohio State University Research Foundation (March 10, 1971).

4. R. W. Staehle, paper presented at the 69th Annual Meeting of the American Society for Testing Materials, Atlantic City (1966).

5. W. E. Berry, E. L. White, and W. K. Boyd, Stress Corrosion Cracking of Sensitized Stainless Steels in Oxygenated High Temperature Water, Corrosion 29(12), 451-469 (December 1973).

6. W. L. Clark and G. M. Gordon, Investigation of Stress Corrosion Susceptibility of Iron-Nickel-Chromium Alloys in Nuclear Reactor Water Environments, Corrosion 29(1), pp. 1-12 (January 1973).

7. L. R. Scharfstein and W. F. Brindley, Chloride Stress Corrosion Cracking of Austenitic Stainless Steel--Effect of Temperature and pH, Corrosion 14, 588t (1958).

8. J. E. Truman and H. W. Kirkby, The Possibility of Service Failure of Stainless Steels by Stress Corrosion Cracking, Metallurgia 72(430), 67-71 (August 1965).

9. W. I. Williams, Chloride and Caustic Stress Corrosion of Austenitic Stainless Steels in Hot Water and Steam, Corrosion 13, 539t (1957).

10. E. E. Denhard, Effect of Composition & Heat Treatment on the Stress Corrosion Cracking of Austenitic Stainless Steels, Corrosion 16, 359-369 (July 1960).

11. T. Baumeister (ed.), Mark's Standard Handbook for Mechanical Engineers, 7th ed., McGraw-Hill Book Co., Inc. New York, pp. 5-66 and 5-67 (1967).

12. F. A. McClintock and A. S. Argon (Eds.), Mechanical Behavior of Materials, Ch. 12, Residual Stress, Addison-Wesley Publishing Co., Inc. (1966).

13. R. M. Latanisian and R. W. Staehle, Stress-Corrosion-Cracking of Iron-Nickel-Chromium Alloys, Proceedings of the Conference on the Fundamental Aspects of Stress Corrosion Cracking at The Ohio State University, Columbus, Ohio, Sept. 11-15, 1967.

14. H. H. Uhlig (Ed.), The Corrosion Handbook, John Wiley and Sons, Inc., p. 164 (1958).

15. ibid., p. 645.

16. R. K. Clarke, J. T. Foley, W. F. Hartman, and D. W. Laron, Severities of Transportation Accidents, SLA-74-000, Vol. 1 through 4 (to be published, (1975).

17. L. B. Shappert, A Guide for the Design, Fabrication, and Operation of Shipping Casks for Nuclear Applications, ORNL-NSR-68 (February 1970).

18. ibid, p. 145.

19. T. I. McSweeney et al., The Risk of Transporting Plutonium Oxide and Liquid Plutonium by Truck, BNWL-1846 (August 1975).

8. SYSTEM ANALYSIS

8.1. Some General System Perspectives

In the previous sections of this report, there have been two major types of systems perspectives: (1) identification of the process phases in canister lifetime, *i.e.*, the description of the sequence of operations involving the waste canister, and (2) identification and analysis of the levels of organization of the containment system, *i.e.*, the components, subsystems, and systems constituting the barriers that prevent radioactivity from being released from the waste-canister-environment complex. Additional system descriptions and analyses are presented here to cover the following topics:

a. Design parameters to control waste temperature, which is a function of waste properties and canister dimensions.

b. A preliminary review of the modes of system failure (based on earlier sections of the report) as related to system design.

c. Consideration of how fission-product cooling times affect reliable containment of radioactivity from the early stages of waste management to ultimate disposition.

d. Characterization of the present state of waste technology in terms of cost analyses reported by others.

e. Consideration of system design factors controlling the stress-corrosion cracking of stainless steel.

f. Consideration of the range of design options within the general reference system, including alternatives in waste form, in canister alloy, in surveillance and monitoring at the RSSF, in shipping mode, in multiple containment, and in remedial actions.

8.2. Reference System Description

The reference system for this study is described in Section 3. This description includes conceptual design and operating procedures for all stages and facilities involved in filling, handling, shipping, and storage of waste canisters. The reference description includes major fabrication and performance standards and the major reference specifications of properties of materials and control temperatures. The numerical reference specifications do not represent an optimum, or even an established system design; they were made specifically for this study, but nevertheless are consistent with available information on the preliminary reference conceptual design of the RSSF and with the aim of high reliability. As is noted in Section 3, there are alternatives and options in the reference system concept for type of coolant, for cooling time, for canister size, and for waste form. This reference system design, with its range of options, is the basis for this consideration of the reliability of aspects of system design.

8.3. Canister Design Parameters for Temperature Control

8.3.1. Heat Conduction in a Cylindrical Canister

In the basic model for temperature within a cylindrical canister of solid high-level waste it is assumed that there is uniform heat generation within a solid and that heat is conducted to the surface of the cylinder where it is dissipated to the environment; that is, there is a specific heat generation rate, a, Btu/(hr)(ft^3) within the solid, which has a thermal conductivity of k, Btu/(hr)(ft)(°F). If end effects are neglected, the heat conduction follows radial paths from the center to the circumference of the circular cross section of the cylindrical container.

The differential equation describing the heat transfer rate in terms of the radial temperature gradient dT/dr at radius r for a cylinder of unit length is

$$q = a\pi r^2$$
$$= 2\pi r \left(-k\frac{dT}{dr}\right) \tag{1}$$

or

$$\frac{dT}{dr} = \frac{ar}{2k} \tag{2}$$

Solution of equation 2 for a solid waste form with no central cavity is

$$T_c - T_s = \frac{ar_s^2}{4k}$$
$$= \Delta T \tag{3}$$

where

T_c = Centerline temperature

T_s = Surface temperature

r_s = Radius of the waste cylinder

If Q is the total heat generation rate per unit length (Q = $\pi r_s^2 a$), equation 3 becomes

$$T_c - T_s = \Delta T = \frac{Q}{4\pi k} \tag{4}$$

which indicates that ΔT is completely determined by Q and k. The volume average of the temperature, $\overline{T}_v$, is obtained from

$$\overline{T}_v = \int T \, dV/(\pi r_s^2) \cdot (1)$$

$$= \frac{\int_0^{r_s} (T_c - \frac{ar^2}{4k}) \, d(\pi r^2)}{\pi r_s^2}$$

$$= \frac{T_c + T_s}{2} \qquad (5)$$

This average temperature is useful for calculating internal pressures.

8.3.2. Use of Internal Fins in a Canister

The purpose of internal fins (cited as an option in Section 3.7.3.) is to provide inner metal "walls" (*i.e.*, fins) to conduct heat directly to the outer canister wall. The thermal conductivity of steel is about 120 times that of calcine, so that a thin cross section of steel can provide a heat-conducting path equivalent to that of a 100-fold larger cross section of calcine. A brief quantitative development of design parameters is given in this section to indicate the feasibility of using internal metal fins to reduce maximum temperatures of solid waste stored in cylindrical canisters.

Using the analysis of Section 8.3.1, we express the difference in temperature between the centerline and the outer surface of the waste solid as follows:

$$T_c - T_s = \Delta T_N$$

$$= \frac{ar_s^2}{4k_N},$$

where the subscript N is used to designate the case of no fins. Thus k_N is the thermal conductivity of the waste solid itself.

We wish to develop a corresponding relationship for the temperature difference with fins, ΔT_F. The thin metal fins are arranged in the canister symmetrically to conduct heat radially from the center to the outer wall of the canister, thus dividing the circular cross section of the waste solid in the canister into segments. It is conservatively assumed that all heat generated in the waste is conducted radially through the fins only. That is, it is assumed that the heat generated in the solid is conducted through the waste itself only at right angles to the radius in a short conductance path to the nearest fin. The radial fins are defined as n in number, t in thickness, and k_F in thermal conductivity. The differential equation describing the heat transfer across any circumference of the circular cross-

section at radius r of a cylinder of unit length is

$$-(nt)k_F\frac{dT_F}{dr} = a\pi r^2 - a(nt)r \tag{1}$$

In equation 1, nt is the total thickness of the fins, such that nt is the cross-sectional area for heat conduction and ntr is the volume of the fins. The right-hand side of equation 1 is the volume of the heat-generating solid (the net capacity of a canister of radius r).

Integrating equation 1 gives

$$\Delta T_F = \frac{ar_s^2}{k_F}\left(\frac{\pi r_s}{3nt} - 1/2\right), \tag{2}$$

where r_s is now the radius of the canister (actually inside radius, since we have neglected heat transfer in the wall of the canister). From equations 1 and 2,

$$\frac{\Delta T_F}{\Delta T_N} = \frac{k_w}{k_F}\left(\frac{4\pi r_s}{3nt} - 2\right) \tag{3}$$

where k_w is the thermal conductivity of the waste (= k_N).

We define the fin factor as

$$1/f = \frac{\Delta T_F}{\Delta T_N} \tag{4}$$

Here, f is a function of the number of fins n, the thickness of each fin t, the ratio of the thermal conductivity of the metal, k_F, to the thermal conductivity of the waste k_w, and the canister radius r_s. The greater the thermal conductivity of the fins, the larger the fin factor. The fraction of the total cross-sectional area of the canister that is taken up by the volume of metal in the fins is given by $nt/\pi r_s$. It is shown below that advantageously high fin factors and reasonably small fractions of volume occupied by fins are practical.

For a representative $k_F/k_w = 100$ and for a fin factor

$$f = 4 = \frac{\Delta T_N}{\Delta T_F},$$

by equation 3

$$1/4 = 1/100 \left(\frac{4\pi r_s}{3nt} - 2 \right)$$

and

$$nt = 0.155 \, r_s.$$

The fraction of the cross-sectional area taken up by the fins is $0.155 \, r_s/\pi r_s$, or 0.049.

For a given canister radius, the volume of contained waste and the total heat generation for the case with fins are slightly smaller than for the case of no fins. For a cylinder of unit length, the volume $V = \pi r^2$, and the effect of small changes in V and r is given by $dV/dr_s = 2\pi r_s$. In proportional terms (*e.g.*, % changes), $d \ln V/d \ln r_s = 2$. This simple relation give a close approximation of the increase in radius of the finned cylinder needed to accommodate the additional 5% of volume to equal the no fin case. That is, when the fins occupy 5% of the canister volume, the radius needs to be increased by 2.5% to give the same volume as for the no fin case. An additional iteration on the calculation taking into account the small change in canister diameter has little effect on the results. Total fin thickness (nt) is now $0.164 \, r_s$ and the cross-sectional area fraction taken up by the fins ($nt/\pi r_s$) is 0.052.

The above general form of the design parameters indicates the feasibility of using fins to give a fourfold reduction in centerline temperature (*i.e.*, $f = \Delta T_N/\Delta T_F = 4$), if the ratio of thermal conductivities is about 100 (*i.e.*, $k_F/k_W = 100$).

8.3.3. Comparison of Design Parameters for Waste Canisters

8.3.3.1. Comparison of Glass and Calcine

A modification of equation 3 utilizes the factor A, the mass-specific rate of heat generation, Btu/hr (per 1 lb fission product oxide), and ρ, the density of oxides in bulk. Thus,

$$\Delta T = \frac{A\rho r^2}{4k} \tag{8}$$

The use of fins with calcine introduces the fin factor, f, that reduces ΔT_C by the factor, f. Thus,

$$\Delta T_C = \frac{A\rho_C r_C^2}{4f k_C} \tag{9}$$

where the above variables have been given subscript C for calcine.

For the glass case, a dilution factor n is introduced:

$$n = \frac{\text{mass of glass form}}{\text{mass of contained fission product oxide}}$$

Thus,

$$\Delta T_G = \frac{\frac{A}{n} \rho_G r_G^2}{4 k_G} \tag{10}$$

which is the form analogous to equation 9, but with subscripts G for glass.

The weight of contained fission products per unit length is

$$\text{For calcine: } W_C = \pi r_C^2 \rho_C \tag{11}$$

$$\text{For glass: } W_G = \frac{\pi r_G^2 \rho_G}{n} \tag{12}$$

Eliminating the r's by combining equations 9 and 11, and 10 and 12, one obtains the maximum weight of fission product oxides (per foot) for a given ΔT

$$\text{For calcine: } W_{C,\,Max} = \frac{4\pi f k_C \Delta T_C}{A} \tag{13}$$

$$\text{For glass: } W_{G,\,Max} = \frac{4\pi k_G \Delta T_G}{A} \tag{14}$$

The ratio of maximum weight of fission product oxides per canister in the glass form to that in the calcine form is obtained by dividing equation 14 by 13

$$\frac{W_{G,\,Max}}{W_{C,\,Max}} = \frac{1}{f} \cdot \frac{k_G}{k_C} \cdot \frac{\Delta T_B}{\Delta T_C} \tag{15}$$

The corresponding volume ratio is

$$\frac{V_{G,\,Max}}{V_{C,\,Max}} = \frac{W_{G,\,Max}}{W_{C,\,Max}} \cdot \frac{\rho_C}{\rho_G} \tag{16}$$

Note that the ratios shown in equations 15 and 16 are not dependent on A, the mass-specific rate of heat generation per pound of fission product oxide.

The calculation of the weight and volume ratios for air and water cooling was made for the following values of the parameters:

	Calcine	Glass
Density, g/cc	$\rho_C = 2.0$	$\rho_G = 4.0$
Thermal conductivity, Btu/(hr)(°F)(ft)	$k_C = 0.2$	$k_G = 0.6$
Fin factor	$f = 1$ (no fins) $f = 4$ (fins)	
Dilution factor	$n = 1$	$n = 3$
Temperature Centerline Maximum, °F	1112	1472
Canister Wall Maximum, °F		
Water Cooling	140	140
Air Cooling	470	470
ΔT Maximum, °F		
Water Cooling	972	1332
Air Cooling	642	1002

The results are as follows:

		Water Cooling	Air Cooling
Ratio,	$\dfrac{\text{Maximum weight of fp oxides in glass}}{\text{Maximum weight of fp oxides in calcine}}$	$\dfrac{4.11}{f}$	$\dfrac{4.68}{f}$
Ratio,	$\dfrac{\text{Volume of fp oxides in glass}}{\text{Volume of fp oxides in calcine}}$	$\dfrac{2.06}{f}$	$\dfrac{2.34}{f}$

The above ratios can be summarized [for the case of no fins ($f = 1$)] as indicating that, at any heating rate and at the specific reference properties, about four times the number of canisters for calcine is required as for glass, and that the volume of each canister for glass is twice that for calcine. If fins are added to the calcine such that the ΔT is reduced by a factor of four ($f = 4$) compared to the case without fins, then the number of canisters for calcine would be reduced to about the same as that for glass.

The analysis above is not intended to be definitive. Rather, it is an illustration of the relation of design parameters on a simplified basis for selected "reference" values of the parameters. A realistic basis would require specification of compositions and properties of "glass" and "calcine," details of canister construction, and definitive temperature limits. At present, these are not available.

8.3.3.2. Comparison of Air Cooling and Water Cooling

The ratio of maximum contained masses of fission products for water cooling to that for air cooling is the ratio of the allowable ΔT's (see equations 13 and 14).

For calcine:

$$\frac{W_{C, \text{ Max, water}}}{W_{C, \text{ Max, air}}} = \frac{972}{642} = 1.51$$

For glass:

$$\frac{W_{G, \text{ Max, water}}}{W_{G, \text{ Max, air}}} = \frac{1332}{1002} = 1.33$$

For a given amount of fission product waste to be stored, the allowable mass of waste per canister is greater for the water-cooled cases, so that fewer canisters are required. Thus, in the case of calcine, the number of canisters required for air cooling is 50% greater than for water cooling and in the case of glass, the number is 33% greater.

8.3.3.3. Effect of Decay Time

For cooling times between 1 and 100 yr, the value of A, the heat generation rate per pound of fission product oxide can be expressed as B/t where B is an appropriate constant and t is cooling time. Thus, on the basis of equations 13 and 14, the maximum weights of oxide in canisters (for both calcine and glass) increase proportionately with cooling time. The absolute effect on maximum waste weight of increasing the cooling time from 1 yr to 10 yr is thus more significant than is the calcine/glass effect.

8.4. Preliminary Identification of Design-Related Modes of System Failures

8.4.1. Introduction

This section identifies the principal modes by which the reference system, as defined in the conceptual reference description, could approach the limiting conditions for specified performance or could, as an extreme, exceed these limits and result in a specific failure. The identification of primary failure modes is related to elements of system design and forms the basis of, but does not constitute, a reliability evaluation. A reliability analysis starts with a "fault tree" or "event tree" for failure events and then goes on to consider secondary effects on the system, common-mode failures, and the fault-correction effects of redundant and back-up features, secondary containment, etc. Reliability evaluation is discussed in Section 9.

A general treatment is given here for cooling in the several stages of storage, shipping, and handling.

8.4.2. Unintended Reduction in Water Flow

In water-basin cooling, a basin contains sealed waste canisters submerged in water. Pumps continuously circulate the basin water in a closed loop through a heat exchanger, where heat is transferred to a secondary water circulatory system with an evaporative cooling tower to discharge heat to the atmosphere. Alternatively, the design of the heat exchanges in the primary

loop may permit it to transfer heat to atmospheric air by either forced or natural convection. This alternative is less typical and probably more expensive than a secondary water circulatory system for a cooling basin with a large heat duty but is attractive for a water-cooled shipping cask.

A failure in water-cooled systems is any circumstance that stops the flow of coolant, *e.g.*, pump failure, major line blockage, or coolant leakage with an inadequate resupply of coolant water. Redundant or standby pumps, as well as basically reliable components, are available as current technology.

A reduction in rate of coolant flow could result in boiling of the water. This would be effective for cooling of the waste canister, since boiling heat transfer coefficients are high. The canister surface temperature would increase to a temperature only a few degrees above the boiling point of water. Such cooling could be continued as long as the steam formed can escape to the atmosphere and the water needed to submerge the canister is available. Boiling water could be used for any phase of waste canister operations where there is a provision for handling the steam.

8.4.3. Unintended Reduction of Air Flow

For air cooling during shipping and storage, a sealed cask surrounding the canister is used. Heat transfer from the solid waste to the external air-cooled surface of the cask is a consideration in cask design.

A reduction in the external air cooling occurs when there is a cessation of air flow by duct blockage or blower failure. As with water cooling, design for component reliability and system redundancy is required. The advantages of a natural convection air-cooled system are cooling simplicity and passivity in that no moving parts or external power are required. This is favorable for reliability.

Air cooling is convenient for in-plant handling and canister transfers, expecially for a canister that contains waste but is not yet sealed. Air cooling can be accomplished by providing a forced draft of ambient or cooled air to the canister surface and a hot-air exhaust system. The hot air may be either discharged after appropriate air cleaning or circulated through heat exchangers for recycle. There is direct operator surveillance for such in-plant operations, but otherwise reliability considerations similar to those for passive storage of waste canisters are followed.

8.4.4. Consequences of Reduced Coolant Flow

The consequence of reduced coolant flow, if extreme enough, is that temperatures of the waste canister and the overpack (if any) would exceed control specifications. The effects of excessive temperature have been discussed in earlier sections of this report. From the standpoint of heat dissipation to the atmosphere, the higher the canister temperature, the greater the rate of heat transfer. Thus, extreme events tend to be self-limiting, although the containment barriers may be impaired by high temperatures.

The extent of damage to the canister by high temperatures is discussed in Sections 6 and 7, dealing with internal and external modes of

attack, respectively. The chief effects are corrosion, internal gas pressuriza-
tion (in the case of calcine) and differential thermal expansion of the solid
waste and canister metal (in the case of glass).

8.4.5. Mechanical Damage

Mechanical damage is associated with impacts of the canister
and objects in its external environment. The types of impact may be classified
as (a) a moving canister striking a stationary object, (b) a stationary
canister being struck by a moving object or (c) both. Basic factors are
the mass of the moving body, the velocity, and the degree of yielding or
energy absorption of either body in a collision. The canister is a schedule
40 stainless steel pipe and has considerable strength against impact. During
shipment, the canister has the massive outer protection of a shipping cask.
During storage the canister is protected against outside influences by a
massive sealed cask or by a massive cooling facility. During in-plant opera-
tions, the handling, transfer, and storage facilities are designed to limit
opportunities for canister damage, especially by dropping or by crushing.
To define and quantify such damage possibilities is not easy. Further dis-
cussion of this subject is given in Section 9. The occurrence of damage
capable of significant waste releases can be made extremely unlikely.

8.5. Reliability Considerations in System Design Options

8.5.1. Background

An objective in the design of a waste management system is to
achieve reliability by giving the as-constructed system the capability of
maintaining its operating integrity over a probable range of varying conditions
and contingencies. The integrity of the containment barriers in the reference
system is chiefly a matter of canister integrity under conditions of stress,
temperature, and chemistry of the coolant environment. In the reference
system design, there is a balance among the following design factors: (a) the
capability of the cooling system to limit temperatures to specified levels,
(b) the rate of heat generation in the waste solid, (c) the strength and
corrosion resistance of the canister alloy, (d) the stability and compatibility
of the waste solid with the canister, and (e) the corrosivity of the coolant
environment to the canister.   As presented in Section 3, the reference design
description is both specific and conceptual. Because it is specific, it does
not fully convey the balancing of design options and safety factors that went
into the design specifications. Because it is conceptual, its descriptions do
not convey the realistic level of construction and operating detail implicit
in the state of technology and which needs to be made explicit in reliability
assessment. Since reliability relates to the probabilities, margins of safety,
and remedial actions of actual system operations, it is appropriate to review
the range of design options and the balancing of the above five major design
factors to provide a perspective on the sensitivity of the overall reliability
to the design options within the scope of the reference system description.
In this section, the emphasis is on general features of cooling systems used
to store canistered waste in relation to reliability.

8.5.2. Fission-Product Age: Near-Term and Ultimate Considerations

Because both the heat generation rate and the radiation hazard
of a waste package are associated with the amount of radioactive material that

has not yet decayed, the potential for temperature or radiation damage decreases with age (total cooling time) of the fission product waste. Heating rates at the reference cooling time of 5 yr are not extreme from the standpoint of engineering heat transfer for fixed cooling systems. But unlike most engineering systems, the heat source cannot be "turned off" as a remedial measure if there is an accidental system malfunction. Also, the presence of significant heat generation (as distinct from sensible heat content) during the transfer of packages from one facility to another is not a common problem for other than radioactive materials. High reliability and low cost (by general industrial standards) is facilitated by reducing the heat generation rate (by prior cooling of waste) for all operations of processing, transfer, and storage of fission product materials.

The common trade-off is between cooling time and cost; further discussion of cooling time strategy is presented below in Section 8.5.3., and the state of technology in relation to cost is presented in Section 8.6. Factors affecting reliability can be summarized thus: Wastes with lower heat generation rates are more passive during storage, and their containment reliability is more readily assured for a wide range of circumstances. The basic strategy of cooling for a long period prior to canister storage is favorable for canister reliability, just as canister storage for ∿100 yr greatly diminishes the difficulty of isolation for longer times.

Although ultimate disposition is beyond the scope of this study of interim storage, the essential continuity of waste management over an indefinitely long time scale makes it appropriate to consider the compatibility of interim storage and ultimate disposition. The following discussion is limited to consideration of fission products only. Any actinides present are an additional source of radioactivity.

After interim storage for 100 yr, the levels of heat generation and radiation of fission products in high-level radioactive waste are reduced by a factor of 100 in comparison to levels at 1 yr age.[1]

The total heat generation from fission products in the spent fuel of a typical light-water power reactor is 3 W/kg total fission products at age 100 yr and 0.0005 W/kg at 1000 yr.[1] These heating levels are practically insignificant. The chief contributors to this low level of heating at 100 yr are, in order of contribution: Ba, Y, Cs, and Sr.

A similar evaluation of the chief contributors to the health hazard from residual fission products may be made in terms of a radiotoxic hazard measure (RHM), defined as the specific nuclide radioactivity per kg of total fission products; this radioactivity is expressed as a multiple of the maximum permissible concentration (MPC) in curies per cubic meter of drinking water.[2] At age 1000 yr, the only significant fission products are I, Tc, Cs, and Zr. The RHM values and weight fractions of the waste for the specific nuclides at 100 and 1000 yr are as follows:

Fission Product Nuclide	Half Life, yr	Fission Product Age			
		100 yr		1000 yr	
		Wt Fraction	RHM[a],m³/kg	Wt Fraction	RHM[a],m³/kg
^{90}Sr	28.1	0.016	4.7×10^8	4×10^{-11}	0.108
^{93}Zr	1.5×10^6	2.6	57	2.6	57
^{99}Tc	2.1×10^5	3.0	1340	2.9	1340
^{129}I	1.7×10^7	0.82	2710	0.82	2710
^{135}Cs	2×10^6	1.1	114	1.1	114
^{137}Cs	30	0.43	1.5×10^8	4×10^{-10}	0.142

[a] Radiotoxic Hazard Measure = Curies per kilogram of fission products ÷ MPC (curies per cubic meter). Values taken from Reference 2.

The potential for health hazard depends on the conditions for water leaching of the radioactive material and the conditions for human ingestion of this water in drinking. If the leaching conditions were such that the ^{129}I in 1 kg of solidified fission products could be leached by a quantity of water larger than 1 m³, for example, 3000 m³, then the concentration of ^{129}I in the water would be less than 1 MPC, and by this criterion, would not be hazardous. The same result would be obtained if the complete leaching were accomplished by only 1 m³ water but in transport to the point of possible drinking, the contaminated water were diluted to 3000 cubic meters. The actual leaching and transport of water depends on the solubility and leachability of the waste solid, the rate of access of ground water, and the transport and dilution of ground water as it moves to the point of possible drinking. Sorption of nuclides on soil surfaces along the transport path is also significant. The design of the waste emplacement is such that such an avenue of human exposure is precluded.

It is apparent that in wastes 100 to 1000 yr old, fission product radioactivity has fallen to insignificant levels; for wastes of this sort, actinides rather than fission products will be of most concern. Although similar storage means may be used for actinides and fission products, only the latter are discussed here in relation to high-level waste.

Interim storage is conceived of as a holding operation on a steady state flow of materials. The size or total waste inventory in an interim storage facility is the product of the rate of arrival and the length of time the waste is held in interim storage. The cooling facilities of the interim facility must have the capability of handling the "hot" new material as well as previously received material for which there is an average rate of heat generation depending on age.

Ultimate disposition differs from interim storage in that (a) the heat generation rates for the former are so low that no special cooling facilities are required and (b) the total inventory is not constant since once

waste is admitted it is not removed. The length of time that integrity is required in ultimate disposition depends on the half-life of the radioactive waste. For most fission products, the time period to nearly complete decay is on the order of a few thousand years. The reliability of the methods and time scale for ultimate dispostion depends mainly on geological knowledge.

The aim of ultimate disposition of waste is to give the waste a form and a location in the earth which will provide geological isolation from the biosphere. Stable, water-excluding subsurface locations such as rock strata or salt deposits are candidate sites. Practical cost considerations indicate that a suitable geological location should be selected rather than elaborately engineered facilities. On the other hand, benefit may be obtained by encapsulating waste canisters in a water-impervious barrier such as rock, concrete, grout, or asphalt. Geochemical considerations are basic to such barrier designs.

From the above considerations, it appears that the major strategies and reliability principles are consistent and compatible both for interim storage of retrievable wastes and for ultimate geological disposition of that waste.

8.5.3. Air Cooling and Water Cooling in General

Water cooling in basins is practical at very high heat fluxes. The water itself constitutes a radiation shield that allows practical visibility and transfers. However, the chemical corrosion possibilities for water cooling and the assurances required to prevent and accommodate any loss of coolant are considerable. At lower heat fluxes especially, where air flow can be provided by natural air convection, the simplicity and passivity of air cooling is clearly more favorable than water cooling to assured reliability, and with less surveillance.

8.5.4. Shipping Criteria

The design problem in shipping is to provide cooling and radiation shielding in a portable assembly which also has sufficient strength to maintain containment of the waste under all probable shipping conditions, including accidents. As discussed above, water cooling is very efficient in space requirements (*i.e.*, compact) and has been adopted in this study as the reference mode of shipping.* However, damage could occur that would result in loss of water coolant and hence in loss of temperature control. For spent fuel shipment, proposed criteria for loss of "external" cooling systems has led to the design of air-cooled casks.

Probably the most favorable of the shipping alternatives, whether in a water- or air-cooled cask, is that based on an extended (10 to 30 years) cooling period before shipping. This scheme could then use water cooling at the processing plant before shipping, shipping in an air-cooled cask, and further air-cooled interim storage at an RSSF; this is a relatively simple system.

Present codes for storage of HLW at reprocessing plants make 10 yr the maximum time of storage before shipment to a waste repository. Since it could be advantageous to store for a period longer than 10 yr before shipping,

---

* However, "wet" shipping is not established by regulation guidelines, nor is it a reference concept for the present RSSF conceptual design.

an alternative of about 30-yr storage at the reprocessing plant is worthy
of consideration. Existing code requirements could be met if the government
maintained on-site interim cooling facilities. If the preshipment cooling
under water continued for 30 yr, subsequent shipping and RSSF storage could
be done with air cooling only.

8.5.5. Solid Waste Forms

The chief limitation of the present reference calcine waste is
that, because it is formed at a lower temperature than is glass, the residual
nitrate and bound water in the calcine product may decompose to gas at higher
storage temperatures, creating internal pressure inside the canister. The
tendency of internal temperatures in the calcine to be higher (compared to
glass) is due to its low thermal conductivity, which is associated with its
unconsolidated state and high void fraction. The low thermal conductivity also
results in large temperature gradients, which create a tendency toward certain
kinds of instability (discussed in Sections 4 and 6). A post-calcination
treatment, such as the addition of low-melting frit to calcine and heating it
in a vented condition until a substantial reduction in porosity has been
achieved, would serve (1) to complete the denitration and dewatering and
(2) to achieve a desirably higher thermal conductivity. Increasing the waste
stability by decomposing and removing residual nitrate and water improves
reliability.

"Densification by vitrification"--the formation of glass waste--
is a post-calcination treatment. However, it is the stability of the glass-
ceramic material, not its low water leachability, which is the measure of
merit for reliable canister containment.

The advantage of vitrification for canister reliability is
chemical stability and inertness and not essentially a matter of the product
being monolithic or noncrystalline. In fact, vitrification carried on in
such a way that molten material contacts the container is likely to be very
corrosive to the container, whether the container is process equipment or a
canister (in case of in-canister glass making). Since vitrification and
various post-calcination treatments are not yet developed sufficiently to
define a reference condition, it suffices here to have indicated the general
issues for reliability.

8.5.6. Surveillance and Monitoring of Waste Canisters in Interim Storage

Remedial or control action based on surveillance and monitoring
is a general aspect of system reliability. Specific responses made to a
system upset could minimize further damage or dispersal. For example, in the
cases of a perforated canister in a water basin or a blocked air passage in
an air-cooled cask, the remedial actions could be retrieval of the package
and repackaging or removal of the blockage. These remedial actions would
supplement the overall reliability of continual containment.

For remedial action, a fault must be detected by surveillance
and monitoring. Canister storage is basically simple enough so that the
surveillance and remedial action strategy is also simple. The design con-
siderations associated with surveillance or remedial action are relevant to

system reliability. A discussion generally applicable to both air-cooled and water-cooled canisters is given below, of the general types of sensing and testing and of the possible application to the several containment barriers (or zones) of the waste-storage system.

The general objectives of surveillance and monitoring are (a) to confirm the maintenance of standard storage procedures and (b) to give information needed as a basis for a decision to overpack defective canisters if circumstances warrant. From a systems viewpoint, the surveillance and monitoring program applies to the various barrier levels of waste confinement: the waste solid, the canister, the overpack (if any), the coolant containment system (if any), and the exclusion area of the storage site. Also, the inspection, detection, measuring, and sampling points are classified as regular and routine or contingent and special.

Although monitoring of the waste packages is provided in the storage facility, it is not considered necessary that the waste solid itself (inside its container) be monitored routinely. Checks of temperature, heat generation rate, radiation level, and external contamination of the canister will be made routinely when the canister is put into storage. The main criterion of containment reliability is that there is no escape of radioactivity into the environment via the coolant. Frequent routine checks of air, surface water, groundwater, and ground surfaces at the site would be likely. Monitoring of water in cooling basins and of air spaces in grouped storage facilities would be essentially continuous. Exit air from open-air sealed storage casks (with overpack and convective air cooling) would be checked for temperature and radioactivity on a statistical sampling basis and/or a relatively infrequent routine basis.

Special monitoring procedures would be imposed upon the detection of leaks, during remedial actions, or in the event of unusual influence on the site, *e.g.*, a flood, tornado, or air crash.

The details of surveillance and monitoring need to be developed for the system as a whole to ensure overall reliability of secure containment and prevention of radioactive releases.

8.6. Review of Cost Analyses for the Current State of Technology of Waste-Storage Systems

8.6.1. Introduction

The review of system design options discussed in Section 8.5 is continued in this section with a change in viewpoint. In the earlier discussion, reliability issues were the focus in the balancing (optimization or "trade-offs") of design factors constituting the current state of technology. In the present discussion, the state of technology itself is the focus, especially with reference to two reported cost evaluations of alternatives for waste management.[3,4] These evaluations are broader than our reference system, but they summarize the work of major programs and are clearly relevant. In addition, a prospective strategy for optimizing the several stages of waste storage is set forth, to aid in developing a reliability viewpoint for our present purposes.

The description of the reference system design is given in Section 3, where the scope of the several stages of canister lifetime and waste management is stated and the range of options as to waste form, coolant, and canister is indicated.

8.6.2. Results of State-of-the-Art Cost Analyses[*]

A review of the extensive studies of waste management at ORNL was presented in 1966.[3] The general conclusions of this study were as follows:

a. The requirement that radioactive wastes be isolated from man's environment is basic. Because of various surveys, ultimate storage in the oceans was considered unacceptable; therefore, the ORNL work was based on dry land storage with isolation from groundwaters.

b. Of the isolated dry land storage concepts, the most economical was a salt mine.

c. Storage in granite is twice as expensive as storage in a salt mine.

d. Engineered storage in concrete vaults is about six times as expensive as storage in a salt mine, but it is still estimated to be less than 1% of the total cost of nuclear electric power.

e. In a dry environment, the calcine form of waste is as acceptable as a glassy solid.

f. For storage in salt, artificial cooling is not required since the temperature can be allowed to rise high enough (900°C for waste solid, 200°C for the salt) to dissipate the heat by natural conduction into the surrounding storage media.

g. The cost of ultimate treatment and disposal of high-level waste is about the same whether it is permanently stored (as liquids or slurries) in tanks, or it is converted to solids and stored in salt.

h. With solidified wastes, the minimum cost occurs if the process wastes can be immediately converted to solids, thereby eliminating liquid storage.

i. The lower leachability of glass in comparison to calcine is not expected to offer sufficient advantage for isolated dry storage, as in a salt mine, to justify a substantial additional cost for vitrification of the calcine.

j. The higher thermal conductivity of glass in comparison to that of calcine is favorable to the early solidification of waste, making it possible to eliminate or to reduce the duration of storage of waste as liquid.

---

[*] Because the technical and economic bases of the references cited in this section are 3 or more years old, numerical values cannot necessarily be considered representative of the 1975 state of the art.

k. A 30-yr interim storage of solid high-level waste in canisters
    in water-filled canals was estimated to cost about one-third
    that for liquid waste in tanks.[3]

A summary of costs estimated for solidification and storage of
calcine and various types of glass was presented by PNL.[4] The costs were
based on a conceptual design of a five tonne per day commercial plant and
include the following solidification products and processes:

a. Calcine product--pot calcination (batch)
b. Glass product
    1. Spray drier with in-pot melting
        (a) Phosphate glass product
        (b) Borosilicate glass product
    2. Spray drier with continuous melter
        (a) Phosphate ceramic product (platinum melter)
        (b) Borosilicate glass product (nonplatinum melter)
            (1) Water cooled only
            (2) Initial water cooling followed by air cooling
                 for an indefinite time

Each of the above concepts was (approximately) optimized for
its design definition. Calculated overall unit costs were all within ±25%
of a median unit cost of 0.03 mil/kWh.* The storage of calcine was as
expensive as the making and storage of glass because the calcine has lower
thermal conductivity and lower temperature limits than glass does. Calcine
requires more cooling or smaller diameter containers, each of which is more
expensive per unit of waste. The lowest-cost case was the continuous melter
concept for borosilicate glass (with water cooling in storage). This solidi-
fication concept has the advantage of being continuous and of permitting the
use of mild steel canisters rather than stainless steel type 304L, which is
specified for in-pot calcination and in-pot glass making.[4]

The above PNL comparative costs include the cost for all interim
cooling required to meet the container heat limitations for salt-mine burial.
It is stated that all the above processes are "essentially ready for commercial
application," but all need further R&D, including that related to materials
and reliability for continuous melters.[4]

8.6.3. Relation of Costs to Design and to System Reliability

The above generalizations as to relative costs of waste manage-
ment options indicate, by the cost "trade-offs," the degree to which the main
system design features reinforce or conflict with one another at the current
state of technology. For example, cooling of waste prior to solidification
reduces the heat generation rate of solidified waste, thereby making reliable
temperature control easier in terms of standard methods. The costs of providing
highly reliable containment of high-level radioactive waste as a liquid solu-
tion must be balanced against the high costs associated with shorter-cooled
waste solid because of the need for (a) many small containers and (b) reli-

_____

*
The cost data, published in 1972, are low. On the basis of 1975 information,
 equivalent costs may be higher by as much as a factor of 10.

able cooling means for the higher heat generation rates. Similar trade-offs between alternative coolants for waste canisters show the balancing of costs and reliability. For the operational phases of waste management (presolidification cooling, shipping, storage, etc.), each design option in current technology has a comparative difficulty in achieving a given level of reliability. The comparative difficulty in current technology is measured by the comparative cost for that design option in reaching the level of reliability. Where cost is a consideration in deciding among options, a thorough reliability analysis (as realistic as possible) is a prerequisite for a meaningful cost comparison. On the other hand, cost analyses, connected as they are to the actual state of technology, direct the application of formal reliability principles to make most effective use of technology already established, and thereby to ease the problem of obtaining detailed evidence required in reliability evaluation by making full use of better-established technology in the overall system design. The design basis of the RSSF is current technology, but not all reliability and cost aspects of waste storage, solidification, shipping, etc., are equally well established.

In this report, the achievement of a quantitative measure of reliability is limited by available level of detail of the system design and by performance data regarding reliability aspects of the present state of technology.

8.6.4. A Simplified Strategy of Optimization

A conceptual strategy of optimization of cost and reliability was constructed on the basis of the following assumptions suggested by the cost considerations:

a. The cost of interim storage capacity of canistered waste per unit weight of fission product waste throughput is directly proportional to the length of time of interim storage, since the size of holdup facilities is proportional to the holdup time.

b. The cost of cooling canistered waste per unit weight of waste is directly proportional to the average heat generation rate in storage.

c. The heat generation rate per unit weight of waste in storage is inversely proportional to the total age of fission products (in the age range of 1 to 100 yr).

Between the age of 1 and 100 yr, the heat generation rate diminishes about two orders of magnitude; over the period of 0.1 to 10,000 yr, the reduction is many orders of magnitude. Engineering optimization of cost and reliability of facilities for storing and handling the waste can only be accomplished practically by dividing the 10,000-yr time period into phases during which the heat generation rate does not change greatly. The reason for this is that if cooling is designed for the heat generation per canister at a certain cooling time (for example, 1-yr cooling), the system will be decidedly overdesigned after ten or one hundred years.

For illustrative purposes, the complete lifetime for waste management is divided into five stages: (1) storage of spent fuel elements

discharged from the reactor, (2) storage of aqueous waste from the fuel reprocessing plant, (3) storage of canistered solid waste in a water basin, (4) air-cooled storage at an RSSF, and (5) ultimate disposition by embedding in a geologically suitable underground location. For each period, the relative cost, R, is given by R = kS/A where S is the length of time of storage in that state, A is the mean age of the waste during that state, and k is a proportionality constant. Considering the mode of decay, a geometric mean age* is used. Assuming that optimization of cost and reliability for each stage will be to the same standard of difficulty in the current state of technology, the storage periods for each stage were determined for the case of approximately equal relative cost for each stage by the above relation. The result, given Table 8.1, shows approximately equal relative costs for

TABLE 8.1. Illustrative Optimization of High-Level Waste Storage
in Five Stages Considering Age of Fission Products

Stage	Stage Description	Waste Age when Entering(yr)	Storage Period (yr)	Mean Age in Stage(yr)	Relative Cost
1	Storage of Spent Fuel	0	2.5	1.6	1.6
2	Storage of Aqueous Waste	2.5	8	5.1	1.6
3	Storage of Canistered Solid Waste in Water	10.5	20	18	1.1
4	Storage of Canistered Solid Waste in Air	30.5	80	58	1.4
5	Ultimate Dry Geological Disposition	110.5	400[a]	238	1.7

[a] Ultimate storage is indefinitely long. The value of 400 years was used for the assumed comparative cost relations.

storage periods of 2.5, 8, 20, 80, and 400 yr for the successive stages. This result used the above assumption of the relation of cost to total fission product age and the same proportionality constant for each stage. For storage alone, the proportionality constant should be higher for the aqueous storage stage, according to the cost generalization stated above. However, considering the high level of radioactivity and the value of unrecovered fissile material in stage 1 and the distributed costs of solidification and shipping in stages 3, 4, and 5, the use of an equal k was considered an appropriate compensation in the present highly simplified indication of overall costs. The use of 238 yr as a mean age for the actually infitely long storage period of stage 5 was considered appropriate, since after about 230 yr of age the residual heating and radioactivity are extremely low (and declining) for all subsequent time in ultimate disposition. (The residual heat and radioactivity for long-term storage was discussed in Section 8.5.)

---

* A log mean is more rigorous conceptually, but the geometric mean is a sufficiently close approximation for the cases illustrated.

8.7. <u>Principal Design Factors Controlling the Time-to-Failure for the Stress-Corrosion Cracking of Stainless Steel</u>

The three general conditions for stress-corrosion cracking are (1) the alloy composition and structure, (2) the corrosive environment (including temperature and oxygen concentration), and (3) the manifestation of stress. The two phases in the interaction of these three conditions to produce failure by stress-corrosion cracking are (1) the initiation and (2) the propagation of cracks. Cracks are by definition nonhomogeneous local structural defects, closely associated with micro-residual stresses and crystal-lattice dislocations involved in deformation.[5] Stress-corrosion cracking of nonsensitized austenitic stainless steel typically occurs as transgranular cracks associated' with deformation, rather than as intergranular cracks which are associated with chemical effects.[6] The higher the degree of sensitization, the greater the degree of intergranular cracking in stress-corrosion cracking. However, the state of corrosion theory and of corrosion control do not allow simple characterization.

Welding produces sharp gradients of stress and deformation that may initiate cracks; crack propagation depends on the balance of crack-healing and crack-propagation conditions.

The safest strategy is very restrictive: the use of (1) fully annealed alloys subjected to minimal deformation and minimal load stress and (2) minimally aggressive environments, including low temperatures, minimal chloride, and minimal oxygen.

Metal composition is a factor. Pure metals[7] and alloys which are not highly passive but which corrode uniformly at rates of greater than 5 mils per year[8] are less susceptible to stress cracking. Also, a temperature of 200°C is more aggressive than lower or higher temperatures,[9,10] presumably because certain healing effects appear at higher temperatures and balance the general increase of chemical corrosive attack. Thus, it would appear that for dilute-water service, austenitic stainless steels, highly immune to common aggressive environments because of special protective surface films, are likely to have rivals from among less passive alloys.

The optimization of reliability and the validation of design requirements appear to call for systematic study and are likely to result in stringent controls via quality-control and quality-assurance programs.

In Section 7, experimental data were reviewed showing quantitative relationships of time-to-cracking as a function of the corrosion variables—chloride concentration, oxygen concentration, temperature, and stress. The quantitative relationships were summarized in Fig. 7.1 through 7.6. The data clearly show that time-to-cracking increases monotonically with decreasing values of the corrosion variables, considered both independently and conjointly. The combined effects of chloride and oxygen concentration, shown in Fig. 7.1 and 7.5, suggest a multiplicative effect when one of the variables is less than 1 ppm and an equivalence effect for concentrations of 10 ppm or more. The interactive effects are not quantitatively shown for other variables, but their joint effects seem to be consistently monotonic. In Fig. 7.4, 7.5, and through 7.6, there appear to be threshold effects, respectively, for temperatures below about 100°C, for chloride and oxygen concentrations below about

1 ppm, and for stress below about 10,000 psi. That is, when all major variables are decreased below these values, the time-to-failure increases exponentially. In practice, this would mean that no failure would occur for values of the variables below this threshold.

Although the above available data are incomplete and inconclusive as to interactive and threshold effects, they do establish a basis for a strategy for seeking relevant data. Such a strategy would include factorial experiments to define interaction and threshold effects for engineering design and for quality standards for the control of corrosion. A brief analysis of the data illustrating such a strategy is given below.

The information presented in Figs. 7.1 through 7.6 may be used to estimate the relation of time-to-failure for each of the four variables. In Fig. 8.1, this extrapolation is shown graphically in a logarithmic plot of time-to-failure *vs.* decreasing values of each of the four corrosion variables: temperature, chloride content of water, oxygen in water, and stress in metal. The point for 1-day failure is taken from the data and corresponds to the values indicated as the abscissa for four variables, considered jointly. Lines with varying slopes are plotted to relate the time-to-failure to one or more controlling variables. The line with the lowest slope (unity) is the line which defines the effect of each variable, considered independently, on the time to failure, based on the shapes of the curves in Figs. 7.1 through 7.6. The numerical values of each variable are stated for the abscissa at positions along the abscissa within the range of the values of the variables indicated in the figures. Thus, the line labelled "single variable controlling" shows the increase in time to failure for each variable independently, based on the relationship suggested by the figures cited. The units for each variable marked at points along the abscissa have this empirical origin, corresponding to decade increases in the time to failure.

If, as the data suggests, the joint effect of the variables is multiplicative, then the effect of reducing each of the four variables by a decade factor would have a combined effect on the time to failure by a factor of $10 \times 10 \times 10 \times 10 = 10^4$. This is indicated by the line with the steepest slope. If the effect of the four variables is not fully multiplicative, the joint effect would be expected to be approximated by one of the lines of intermediate slope. For temperatures below 100°C, chloride and oxygen concentrations below 5 ppm, and stress below 10,000 psi, the time to failure would be increased from 1 day to more than 10^5 days.

As stated previously, such an extrapolation can be considered only as illustrative and not established by the available data. However, evidence bearing on this hypothesis could be obtained from a suitable experimental program.

The importance of sensitization should also be noted. The high rates of corrosion in the data used above were partly due to a sensitized condition of the stainless steel. In the absence of sensitization, the time to failure would be expected to be increased by one order of magnitude (at least) for the corrosive effect of a given concentration of oxygen and chloride.

8.8. Identification of State-of-the-Art Alternative Materials of Construction

Five generic metal alloys have been selected that are well established in the state of the art for containment under the reference storage conditions

	Reference Condition				
Temperature, °C:	>200	~120	~110	~100	~90
Chloride, ppm:	~10	~1	~0.1	~0.01	-
Oxygen, ppm:	~10	~1	~0.1	~0.01	-
Stress, psi:	>2 x 10^4	~10^4	~5 x 10^3	-	-
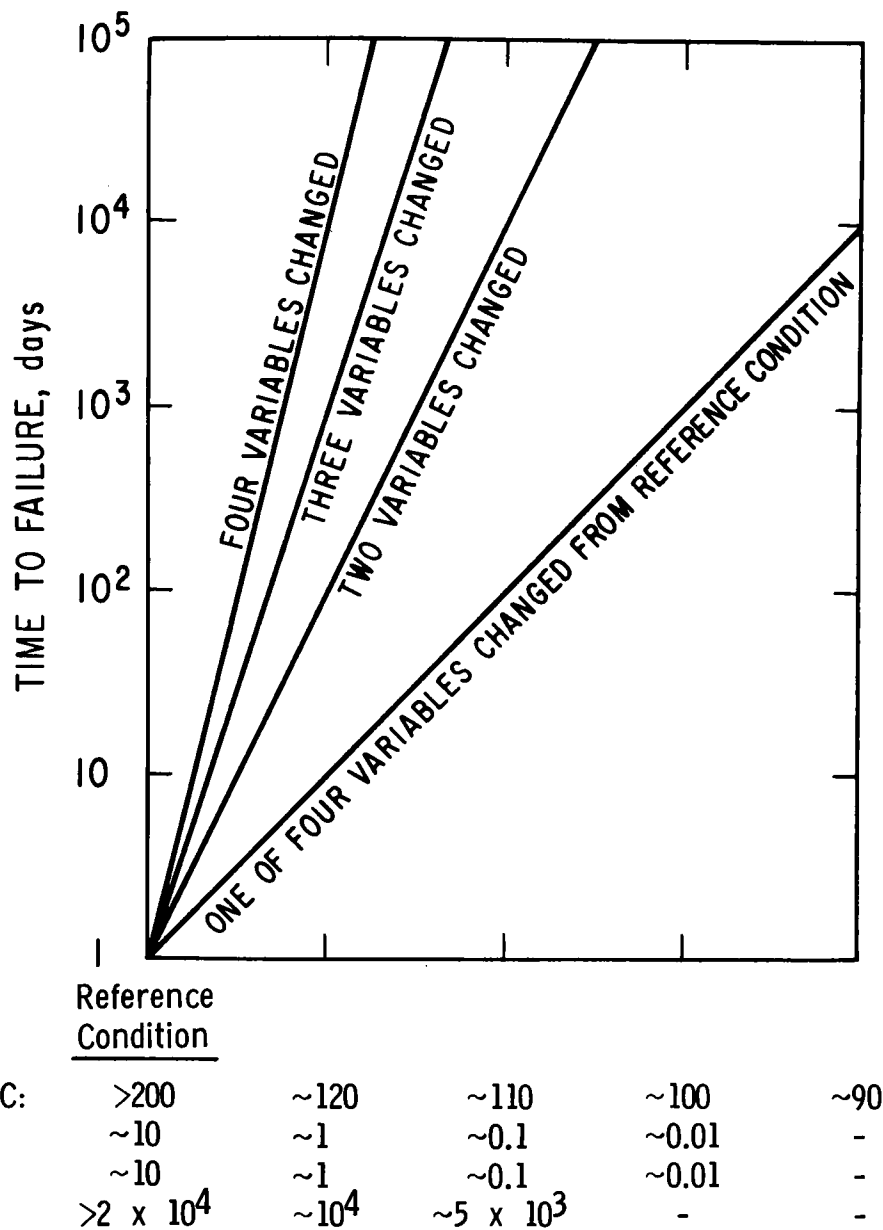
Fig. 8.1. Model Illustrating Factor Analysis of Corrosion Data for Application to Reliability Evaluations (based on effects shown in Fig. 7.1 through 7.6).

in air and water environments. These generic alloys and representative specific alloys are believed adequate to provide a background perspective for the selection of a reference material. The alloys selected are as follows:

a. Austenitic stainless steels, represented by type 304L.
b. Carbon steels, represented by low-carbon steel 1010.
c. Ferritic stainless steels, represented by type 430.
d. Incoloy (Ni-Fe-Cr) alloys, represented by Incoloy 800 and Incoloy 825.
e. Inconel (Ni-Cr) alloys, represented by Inconel 600.

The compositions and representative room temperature properties are summarized in Table 8.2. The mechanical properties are all quite similar at ambient temperatures, although the carbon steel has comparatively inferior properties at elevated temperatures.

Because of the present emphasis on assessment of the importance of stress-corrosion cracking, a rating[11] of the relative resistance of the above alloys to this type of corrosion is presented in Table 8.3. Low-carbon steel was not among the alloys tested; however, it is not susceptible to chloride-induced cracking in water environments. Water service for low-carbon steel is principally limited by oxygen concentration. Its satisfactory performance depends on low oxygen concentration, low temperature, and suitable additives and inhibitors in the water, in accordance with boiler practice.

Table 8.3 shows a relatively superior rating for Inconel and stainless steel type 430 in resistance to a specific high chloride, high stress attack. However, an overall evaluation of alloys would have to consider other modes of failure and other exposure conditions, closer to those of the reference system. For example SS type 430 is susceptible to pitting and to crevice corrosion under some conditions.

The present reference design calls provisionally for stainless steel type 304L as canister material. The purpose of the present identification of generic alternatives is not to put forward alternatives for the design, but to present a perspective for the present reference design. In the selection of canister material, exposure in processing and shipping environments, as well as storage conditions, must be considered.

The approximate current prices of the above alloys are presented in Table 8.4. Stainless steel type 304L occupies an intermediate position in the 18-fold range of unit prices. From this simplified and incomplete viewpoint, it appears that alloys other than stainless steel 304L are candidate metals that are economically and technically adequate.

TABLE 8.2. Properties and Compositions of Selected Alloys

Alloy	Composition (wt%)					Room-Temperature Properties			
	Cr	Ni	Fe	C	Other	E^a (psi)	Yield Stress (psi)	Ultimate Stress (psi)	Elongation (%)
Carbon Steel 1010	–	–	∿100	0.08–0.13	0.3–0.6 Mn, 0.04 Max P, 0.05 Max S,	29×10^6	55,000	67,000	25.
Ferritic Stainless Steel Type 430	14–18	–	balance (∿82)	0.12	1 Si max 1.0 Mo max	29×10^6	45,000	75,000	30.
Austenitic Stainless Steel Type 304L	18–20	8–12	balance (∿70)	0.03 max	2 Mn	28.5×10^6	30,000	80,000	55.
Incoloy 800	21.0	32.5	46.0	–	0.38 Al 0.38 Ti	28.5×10^6	30,000	75,000	50.
Incoloy 825	30.0	42.0	30.0	–	0.10 Al 0.90 Ti 3.0 Mo 2.25 Cu	28.3×10^6	44,000	100,000	43.
Inconel 600	15.5	76	8.0	–	–	31.0×10^6	30,000	80,000	55.

[a] Modulus of elasticity.

TABLE 8.3. Classification of Alloys According to Cracking
Behavior in Boiling 42% $MgCl_2$[11]

Reference: U-Bend specimens stressed beyond
Yield, hole drilled at apex.

Less than 1 Day	10-55 Days	No Cracks in 55 Days
SS Type 304	Incoloy 804	Inconel 600
304 (sensitized)		
304L	Incoloy 825	SS type 430
Incoloy 800		

TABLE 8.4. Prices of Selected Alloys

Reference: Base price[a] from Chicago
distributor Feb. 3, 1975,
for 3/8-in. plate, fully
annealed.

Alloy	Approximate Price ($/lb)	Relative Unit Price	
		A	B
Carbon Steel, 1010	0.18	1	0.21
Stainless steel, type 430	0.65	3.6	0.76
Stainless steel, type 304L	0.85	4.7	1
Incoloy 800	2.25	12.5	2.6
Incoloy 825	3.13	14.9	3.7
Inconel 600	3.25	18.0	3.8

[a] The price of plate stock does not constitute an estimate
of canister cost, which involves forming, welding, heat
treatment, surface cleaning, quality assurance, commer-
cial availability, etc.

References for Section 8

1. *Siting of Fuel Reprocessing Plants and Waste Management Facilities*, compiled and edited by the staff of Oak Ridge National Laboratory, ORNL - 4451, Table 3.11 (July 1970).

2. J. Hamstra, *Radiotoxic Hazard Measure for Buried Solid Radioactive Waste*, Nucl. Safety 16(2), 180-189 (March-April 1975).

3. R. E. Blanco, J. O. Blomeke, and J. T. Roberts, *Future Magnitudes and Proposed Solutions of the Waste Disposal Problem*, CONF-660208, Proceedings of the Symposium of the Solidification and Long-Term Storage of Highly Radioactive Wastes, February 14-18, 1966, Richland, Washington, pp. 3-16 (1966).

4. J. L. McElroy *et al.*, *Evaluation of WSEP High-Level Waste Solidification Processes*, BNWL-1667 (July 1972).

5. D. Birchon and G. C. Booth, *Stress Corrosion Cracking of Some Austenitic Steels*, 2nd International Congress on Metallic Corrosion, New York, New York, March 11-15, 1963.

6. P. R. Swann, *Stress-Corrosion Failure*, Scientific American, 214(2), 73-81 (February 1966).

7. J. E. Truman and H. W. Kirkby, *The Possibility of Service Failure of Stainless Steels by Stress Corrosion Cracking*, Metallurgia 72(430), 67-71 (August 1965).

8. R. W. Staehle, *Comments on the History, Engineering, and Science of Stress Corrosion Cracking*, in Proceedings of a Conference on the Fundamental Aspects of Stress Corrosion Cracking, The Ohio State University, September 11-15, 1967.

9. R. M. Latanision and R. W. Staehle, *Stress Corrosion Cracking of Iron-Nickel-Chromium Alloys*, Proceedings of Conference, Fundamental Aspects of Stress Corrosion Cracking, The Ohio State University, Columbus, Ohio, pp. 214-300 (September 11-15, 1967).

10. J. W. Frey and R. W. Staehle, *Effect of Temperature, Stress, and Alloy Composition on the Role of Stress Corrosion Cracking in Fe-Ni-Cr Alloys*, Presented at the 23rd NACE Conference, March 16, 1967, pp. 35-41.

11. G. E. Moeller, *Understanding Stress Corrosion Cracking*, Proceedings, 3rd Western States Corrosion Seminar, NACE, May 6-8, 1969, San Dimas, California (reprinted by International Nickel Co.).

9. CONSIDERATIONS FOR ESTABLISHING RELIABILITY

9.1. Review of Reliability Methodology

9.1.1. General Objectives of Reliability Analysis[1-7]

Reliability, defined quantitatively, is the probability that a specified unit will perform satisfactorily for a specified period under specified operating conditions. Formal reliability analysis incorporates probabilistic measures to rationalize uncertainties insofar as possible and incorporates methods of systems analysis and decision theory to illuminate the administrative and design choices. The aim of reliability analysis is to answer the overall question of whether reliability is satisfactory. Reliability evaluation is confined to engineering or technical performance of systems, which normally does not include the consequences in terms of hazards, costs, or benefits of system function or malfunction.

Reliability includes quality control considerations as elements of system design, but focuses on performance of system design alternatives, rather than being restricted to qualification of material input or of administrative procedures of the system.

In describing the reliability of a given system, it is necessary to specify (1) the equipment failure process, (2) the system configuration which describes how the equipment is connected and the rules of operation, and (3) the state in which the system is to be defined as failed. The repair mechanism is also considered for maintained systems.

Analysis of failure modes and effects is carried out systematically under the guidance of a fault tree, in which the failed condition is first defined and then all pathways leading up to the failed condition are laid out sequentially for the various system components and circumstances of operation.

In general, there are two ways of constructing a mathematical distribution of system failures. One is to use empirical evidence from components used in a similar manner, with deductions from established first principles to interpret the effects of minor dissimilarities. The other, in the absence of direct empirical evidence, is to use physical reasoning entirely to hypothesize a system from first principles. Clearly, a combination of these two approaches is desirable for reliability analysis of proposed new designs.

The focus of this analysis is on the reliability of the primary waste container--the metal canister--as an impermeable barrier enclosing the solid waste. The environment of the canister wall is twofold: (a) inside is the waste, which is a source of thermal, chemical, or mechanical effects; (b) outside is the coolant and external sources of possible effects. Also involved are the metallurgical characteristics and history of the canister metal. The secondary containment controls the immediate external environment of the canister, protecting the canister from other exterior influences. The chief processes affecting reliability are corrosion phenomena.

In addition to establishing an overall probability measure, the reliability analysis is expected to have use in the identification of those

steps leading to high failure rates, and to lead to recommendations to modify
the reference system to ameliorate the high rates. Reliability probabilities
are also important for evaluating alternative designs and for contributing
key information for overall risk evaluation.

9.1.2. Fault Tree Analysis

The major application of formal reliability methodology is by
the construction and analysis of a fault tree which includes all modes of
potential system failure. The ability to make complete, absolute, quantitative
probability estimates is implied in the analysis, but useful results may be
obtained for partial or comparative (relative or ranked) probability estimates.

9.2. Mathematical Probability Functions in Reliability Analysis

In order to establish the degree of reliability and to make comparisons
of reliability data, quantitative measures of reliability are required. In
the present study, such measures are used only conceptually and implicitly--
that is, quantitative reliabilities have not been developed for the reference
system. However, for further definition of reliabilities it would be desirable
to use more explicitly the quantitative formulations of modern reliability
theory and technology. In this section, we wish to identify the mathematical
functions of probability measure which are most widely used in reliability
analysis and which have potential use in application to canister reliability.

9.2.1. General Probabilistic Analysis Related to Corrosion

Since reliability is equivalent to nonfailure, the sum of the
probability of reliable operation and the probability of failure in operation
is unity. Fault trees and event trees describe the relation of failure pro-
pagation of components to system failure. A related reliability measure is
the frequency of failures or the expected failures in a given time.

The analysis of fatigue failures (including corrosion fatigue)
has made important use of probabilistic analysis. Here the analysis concerns
local defects which may be inhomogeneously distributed. Probabilistic analysis
appears to be relevant to corrosion where localized attack or structural defects
are involved. This is likely in aspects of stress-corrosion cracking. A general
case for the probabilistic view of corrosion has been proposed by Evans,[8] who
distinguishes between "corrosion velocity" and "corrosion probability." Among
other considerations, he discusses the use of a corrosion inhibitor "such as
to reduce the virtual expectation to one point of attack per square foot." This
is a probability frequency on a surface area basis, and clearly a large surface
has a greater chance of undergoing attack (failure) than a small surface, such
as is convenient for laboratory tests. He suggests the joint use of statistical
analysis and dimensional (model) analysis in order to predict large-scale effects
from laboratory data.[8]

In data obtained for stress-corrosion cracking and reviewed in
Section 7, the time-to-failure was the prime measure of corrosion; the scatter
of data was considerable. Inhomogeneities of structure and composition, grain
boundary effects, and local residual stresses are involved in this mode of

corrosion. Although the present aim is to identify conditions of practical immunity to attack rather than quantitative precision in characterizing attack, the desirable final characterization of system reliability would be in quantitative terms of a minimum (acceptable) reliability which, stated in general terms, would be equivalent to a probabilistic failure rate.

9.2.2. Continuous and Discrete Probabilities

Although canister failures themselves are discrete events, the overall probability analysis is concerned with the factors defining the exposure, the resistance to corrosion, and times to failure. All of these are continuous random variables. Therefore, a probability function of the continuous, rather than the discrete, type will be required.

9.2.3. Significance of Mathematical Formulations of Reliability

At present, the emphasis in assessing reliability of interim waste storage systems is concerned with engineering design of failure-free systems rather than with statistical analysis of data obtained from experience. The state of design has not yet advanced to the point of systems analysis (wherein, for example, the frequency of failures is assessed in terms of the capability of remedial action) or to the point of establishing the statistical aspects of quality-control specifications. Therefore, mathematical formulation of reliability is not applicable to high-level waste canisters at this stage of development of waste management and associated sciences. However, further detailed design of waste management systems, analysis of operating data, further developments in corrosion theory, development of QC and QA systems, and continuing studies of reliability and risk can be expected to take an increasingly mathematical form, thus improving the bases for quantitative estimates of reliability.

9.3. Factors Controlling the Consequences in Abnormal Conditions of Solid Waste in Retrievable Storage

The reference design adopted in this study specifies maximum allowable centerline temperatures for the solid waste stored in canisters. Temperatures for the calcine form and the glass form are selected on different bases.

In the case of solid glass, canister reliability could be affected by direct attack at the interface or by pressures initiated in the interior and transmitted to the canister wall. Under normal conditions, a temperature gradient exists across the glass cylinder, with low temperatures at the canister wall. Loss of cooling would result in elevating the temperature both at the wall and at the centerline. Although temperature elevation may result in the glass melting at the center, melting at the canister wall would not be expected. Glass-canister reactions (though low at normal conditions) could be expected to increase at the elevated temperature, but no data is available to indicate whether this would be serious.

Internal mechanical pressures may be generated by thermal expansion of the glass if the temperature of the glass rises more rapidly than does that of the canister. If the temperature increases throughout the entire canister are uniform during an excursion, no stresses would develop in the canister

because the thermal expansion of the canister is greater than that of the glass. Some pressure of the expanding glass would be relieved by flow rather than being transmitted to adjacent cooler glass and the canister wall. Apparently, canister reliability is not likely to be compromised, but this needs to be demonstrated.

Higher temperatures can result in crystallization (devitrification) and phase segregation in glass. Although this consequence would alter its chemical nature and could increase its direct leachability in water, it would not directly affect the reliability of its containment in a canister. Crystallization of glass is accompanied by increases of both density and thermal conductivity. These effects would have a tendency to reduce stress on the canister.

The allowable limits directly affecting canister reliability are canister wall temperatures and internal gas pressures, rather than interior temperatures of the waste solid. Optimal design and reliability controls should consider these aspects in connection with the specification of waste glass composition.

In the case of calcine waste, some of the same principles are involved; however, the effects of increasing temperature on the porous, poorly consolidated calcine are quite different from those on monolithic glass. Increasing the centerline temperature of calcine results in sintering and in decomposition of residual nitrates and moisture. Sintering is partial fusion, which is manifested by a reduction in porosity and in densification. A marked increase in bulk thermal conductivity is expected, with an initial coefficient perhaps as low as 0.15 Btu/(hr)(ft)(°F) for porous granular material possibly increasing to 1.5 or higher for fused crystalline material. This would decrease the radial temperature gradient of the waste and have the desirable effect of lowering the centerline temperature. If there is adequate exterior cooling of the canister, sintering of the calcine would occur at the center, and a zone of unsintered calcine would exist near the cooler wall. The volume changes as a result of crystal transformations, the volume expansion of the solid at higher temperatures, and even the volume expansion on phase change to liquid are smaller than the fraction of voids present in the unconsolidated material. Thus it is expected that there would be no net expansion that might endanger the canister, and sintering may be accompanied by formation of a central void.

It may be desirable to add an inert ingredient, a frit, to the calcine to make the sintering effects more uniform.

The basis for the temperature limit on calcine is not sintering, but pressurization of the gas space in the canister as a result of the temperature increase of gas in the voids and by gasification of contained water and nitrate in the calcine. However, the contained calcine could be safely exposed to a high internal temperature before sealing of the canister; then any subsequent high temperatures during storage should not be deleterious.

Thus, final determination of adequate reliability controls for calcine storage requires the specification of wall temperatures and temperature stability conditions for the particular composition and initial thermal treatments of the waste.

9.4. Applicability of ASME Boiler and Pressure Vessel Code[9]

The applicability of the ASME Boiler and Pressure Vessel Code to the fabrication and use of stainless steel type 304L waste canisters was examined. In view of the complexity, volume, and numerous subject areas of the code, a thorough examination within the constraints of time and effort was not possible. Observations made are discussed below.

The code is intended principally for application to vessels, valves, piping, and other components of the nuclear energy system of any power plant. Its inapplicability to structures such as waste canisters may be inferred from the following quotation taken from the Code: "Specifically excluded from consideration in this section [Section III] of the Code are tubes or other forms of sheathing used only for cladding nuclear fuel or neutron control material."[10] Further, the Code does not take into account "deterioration which may occur in service as a result of radiation effects, corrosion, erosion, or instability of the material."[11] In spite of the intent of the Code, its possible application to waste canisters was examined.

The Classes and Rules examined were those of Division 1 and Class 1. Division 1 includes provisions for metal structures; rules for Class 1 are the most stringent in the Division.

The rules for Division 1, Class 1 as originally published[9] cannot be used for austenitic stainless steels and high-nickel alloys when items are subjected to metal temperatures in excess of 800°F (427°C).[12] Reference 12 includes design stress intensity values up to that temperature. Subsequent to the issue of reference 9, Code Case 1592 was approved and issued.[13] This case extended design stress intensity values for many austenitic stainless steels and high-nickel alloys to higher temperatures (depending on the alloy), but with additional restrictions on time of exposure. Stainless steel type 304L is not included by Code Case 1592, and hence 800°F remains the upper limit if Code requirements are to be met.

As an illustration of temperature extensions included in Code Case 1592, data for stainless steel type 304 is shown in Table 9.1. The maximum temperature has been extended to 1500°F (816°C), but the allowable stress intensity varies considerably with the design time of exposure: 7900 psi for 1 hr to 600 psi for 350,000 hr.

For the case in which the canister is to contain high-level waste in the glass form, the highest temperature of exposure for the canister occurs during the filling operation: 950 to 1000°C. This far exceeds the maximum temperature of 800°F (427°C) for stainless steel type 304L and also exceeds that of 1500°F (816°C) for stainless steel type 304 specified by Section III of the Code. For canisters containing high-level waste in the calcine form, filling could be performed at temperatures below 800°F (427°C) if proper control is exercised for the operation.

All other reference operations up through shipment to the RSSF are conducted under water, and the resulting temperatures are compatible with the Code. Even if storage at the RSSF is conducted according to either of the air-cooled concepts, the canister wall temperatures will be below 810°F (432°C).

TABLE 9.1. Allowable Stress[a] of Stainless Steel Type 304
as a Function of Temperature and Time[14]

Temp.(°F)	1 hr	10 hr	30 hr	10^2 hr	3×10^2 hr	10^3 hr	3×10^3 hr	10^4 hr	3×10^4 hr	10^5 hr	3×10^5 hr
800	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4
850	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	19.9	19.8	19.3
900	19.6	19.6	19.5	19.5	19.4	19.2	18.8	18.5	18.3	17.7	16.0
950	19.1	19.1	19.0	18.7	18.2	17.5	17.2	16.9	16.2	14.2	12.2
1000	18.5	18.4	17.8	16.9	16.2	15.9	15.5	14.7	13.1	11.1	9.3
1050	18.0	17.7	17.1	16.2	15.5	14.9	14.1	12.2	10.3	8.7	7.3
1100	17.6	17.1	16.3	15.3	14.5	13.5	11.5	9.7	8.2	6.8	5.7
1150	17.0	15.7	14.8	13.8	12.9	11.0	9.3	7.7	6.4	5.3	4.4
1200	16.0	14.2	13.3	12.2	10.6	8.9	7.4	6.1	5.1	4.1	3.4
1250	14.7	12.9	11.9	10.3	8.7	7.2	5.9	4.9	4.0	3.2	2.7
1300	13.4	11.4	10.0	8.5	7.0	5.9	4.8	3.9	3.2	2.5	2.1
1350	12.2	9.7	8.4	7.1	5.9	4.8	3.9	3.1	2.5	2.0	1.6
1400	10.8	8.1	6.9	5.9	4.8	3.9	3.1	2.5	2.0	1.6	1.2
1450	9.3	6.8	5.9	4.6	3.8	3.0	2.4	1.9	1.5	1.2	0.9
1500	7.9	5.3	4.4	3.5	2.8	2.2	1.7	1.3	1.0	0.8	0.6

[a] Stated in units of 10^3 lbs/in^2.

The rules of the Code for welding are voluminous and cover many different subject areas. In any welding performed on the canister during its fabrication prior to filling with waste there should be no difficulties to meeting the Code requirements. The final closure weld will, however, need to be effected remotely because of the high radiation field. Whether all rules of the Code can be met under these conditions will require a very careful evaluation by persons competent in remote welding. A particularly difficult area is the qualification of closure welds according to Chapter IX of the Code. Radiographic inspection, acceptable to the Code if performed under prescribed conditions, cannot readily be performed in a high radiation field.

Reference for Section 9

1. T. H. Bompas-Smith, Mechanical Survival: The Use of Reliability Data, McGraw-Hill Book Co., UK (1973).

2. R. H. W. Brook, Reliability Concepts in Engineering Manufacture, Butterworths, London (1972).

3. A. E. Green and A. J. Bourne, Reliability Technology, Wiley-Interscience (1972).

4. G. H. Sandler, System Reliability Engineering, Prentice-Hall, Inc. (1972).

5. M. L. Shooman, Probabilistic Reliability: An Engineering Approach, McGraw-Hill Book Co. (1968).

6. K. J. Schneider and A. M. Platt, High-Level Waste Management Alternatives, BNWL-1900, Vol. 1 Summary; Background and Data Base; Evaluation Methodology (May 1974).

7. Igor Bazovsky, Reliability Theory and Practice, Prentice-Hall, Inc. (1961).

8. U. R. Evans, The Corrosion and Oxidation of Metals: First Supplementary Volume, Edward Arnold Publishers (1968).

9. ASME Boiler and Pressure Vessel Code, Section III, Nuclear Power Plant Components, American Society of Mechanical Engineers, New York (1974).

10. ibid., footnote 4 of paragraph NA-1110.

11. ibid., paragraph NA-1130.

12. ibid., Appendix I, Table I-1.2.

13. ASME Boiler and Pressure Vessel Code, 1974 Code Cases, American Society of Mechanical Engineers, New York, Code Case 1592 (July 1, 1974).

14. ibid., Table I-14.4A.

10. CONCLUSIONS AND RECOMMENDATIONS

10.1. Introduction

The assessment of canister reliability for the reference system comprised

a. a detailed consideration of the materials involved--the canister and the waste solid--based on chemical and metallurgical composition;

b. consideration of the major features and conditions of the systems (*i.e.*, facilities) involved in canister handling, storage, and shipping;

c. very little consideration of the design principles, alternatives, or optimization of either the facilities or the processes involved, even though the solidification process, for example, is highly determinative of the reference specifications for the waste and canister materials and for the temperature and other system specifications.

10.2. Questions Pertaining to Temperature Control

In the several phases of canister life, the control of temperature was the basic requirement of system design and the basic determinant of canister performance. The key role of temperature extends from the earliest exposure of the canister to high temperatures in fabrication and heat treating, through the filling and handling operations associated with solidification, and in all normal or abnormal conditions in shipping, as well as in all storage operations. Greater stability is conferred on the solid waste form (calcine or glass) by high-temperature equilibration before sealing in the canister, but operability of the solidification process equipment and integrity of the canister during filling and sealing tend to be adversely affected by the high temperatures encountered during these same operations. The absence of a definitive basis of temperature control throughout the waste-canister lifetime is a major obstacle to determining quantitative or assured reliability. Of course, a definitive basis for temperature involves the interactive effects of materials chemistry, system design, and solidification process operation.

10.3. Conclusions

10.3.1. Conclusions Pertaining to Calcine and Glass

a. The reference concept of interim retrievable storage of solid high-level waste (glass or calcine) in metal canisters, cooled in air and/or water for periods of up to 100 yr or more, appears inherently capable of being implemented with practical canister reliability, approximately within the present state of technology. More precisely, if the specific reference canister (SS 304L) is held strictly within the temperature limits specified in Section 3 and if all other features of the system are designed to achieve the best state-of-the-art performance compatible with these temperature limits, the reference canister has the inherent capability of achieving highly reliable performance.

However, critical reservations remain as to the degree of reliability of the reference system, especially as regards possible options, the details of implementation, and the basis of regulatory approval.

b. The reliability of canisters fabricated of stainless steel type 304L and used in conformity with the reference conditions may, in fact, prove to be sufficient. However, there is insufficient quantitative information supporting such a conclusion.

c. The reference design is not detailed or firm enough at this time to identify clearly the bases for choices of design from among state-of-the-art options or for the specifications for quality control of high-performance canister material. Similar deficiencies are noted for the conditions during transportation of high-level wastes.

d. Insufficient information is available on basic, long-term properties of the waste forms and their interactions with canister materials.

e. Current information from corrosion science, including consultations with experts such as Professor Staehle, is insufficient to allow behavior to be predicted for prolonged periods under very mild conditions. The absence of empirical test results and lack of adequate theoretical bases of such phenomena as stress corrosion (for materials susceptible to it) inhibits the development of "good" designs.

f. Although reliability analyses have been applied practically and successfully in several industries, no applications to chemical corrosion or radiochemical systems for extended periods have yet been reported.

g. Because the reference conditions for the purposes of this report (temperatures, heat loadings) for shipment in water-cooled casks are similar to those for storage underwater at the reprocessing plant, all wastes (both calcine and glass) can be shipped shortly after the canisters are filled, without exceeding temperature limitations. Glass, and calcine contained in fin-equipped canisters, can be shipped in air-cooled casks after waste cooling times of 10 yr. Calcine contained in canisters having no fins must be cooled 14 to 18 yr before shipment.

h. The alternative concept of shipping glass or calcine in air-cooled casks may not be compatible with subsequent storage at the RSSF using the Water Basin Concept because the high canister wall temperatures during shipment may lead to sensitization of the canister material.

i. The centerline temperature limitations for glass and calcine may be excessively restrictive. Since waste in the central regions of a vented canister does not directly affect the canister wall, reliability may not be compromised by allowing higher central temperatures (by increasing the canister diameter) and letting the nonsealed (vented) canister reach equilibrium relative to off-gassing before effecting the final closure. During the off-gassing period, waste in the calcine form may consolidate, thereby improving its thermal properties. Waste contacting the canister wall would not be affected.

j. A brief review indicates that the Rules of the ASME Boiler and Pressure Vessel Code, Section III, cannot be used for stainless steel type 304L canisters because of the inability to qualify the final closure welds and (in the case of the glass waste form) because of excessive temperatures during reference filling operations.

10.3.2. Conclusions Pertaining to Glass

a. With the restriction that canister diameters cannot exceed 6 in., the reference concept of preparing solidified waste and filling canisters at a waste cooling time of one year can be readily implemented for waste in the glass form.

b. Because of high stresses induced in canisters that contain glass, the control of temperature and water purity during underwater operations [storage at the reprocessing plant, water-cooled shipment, storage at the RSSF (Water-Basin Concept)] is highly germane to maintaining canister reliability. In case of higher than anticipated failure rates, surveillance and remedial action would be used to prevent release of radioactivity.

c. The concern over high stresses in canisters containing waste in the glass form can be reduced by several options that include:

1. Elimination of water cooling at all stages after the filling of canisters;

2. The addition of a stress-relieved overpack;

3. Precasting of the glass form before it is introduced into the canister;

4. Stress-relieving treatment of the filled canister, such as the subcooling method described in Section 3;

5. Stress-relieving treatment (such as shot peening) of canister surfaces;

6. Use of an alternative alloy not sensitive to stress corrosion cracking.

d. The transition from metastable glass to crystalline form (vitrification) is accompanied by increases in density and thermal conductivity that enhance the transfer of heat.

10.3.3. Conclusions Pertaining to Calcine

a. With the restriction that canister diameters cannot exceed 6 in., only if internal fins are used in the canister can the reference concept of preparing waste and filling canisters at a cooling time of one year be implemented for calcine. For canisters that do not contain fins, calcine preparation must be delayed until cooling has continued for 2 1/2 to 4 yr.

b. Inadvertent increases of temperature of calcine are accompanied by increases in density and thermal conductivity, enhancing heat transfer and tending to compensate for and limit the temperature rise.

c. Post-treatment of calcine at 800°C is provided as part of the reference concept to reduce the nitrate and moisture residuals. Treatments at even higher temperatures, perhaps 1000°C, would effect consolidation of the calcine. This would tend to overcome several of the adverse characteristics of unconsolidated material: low thermal compatibility, low bulk density, high surface area, relatively high solubility and leachability, and ease of dispersion due to lack of consolidation. An additional benefit of consolidation would be the (probable) reduced mobility of migrating fission products such as cesium. Consolidation would be further enchanced by additives, such as silicates, to provide local (interstitial) molten phases that aid in sintering. To avoid sensitization and stress effects on canisters, such consolidation could be done in separate vessels; alternatively, the canisters could be overpacked.

d. The use of fins to reduce centerline temperatures in canisters that contain calcine or, alternatively, to allow larger canister sizes is quite feasible. Metallic fins occupying about five percent of a canister cross section reduce the temperature difference across the waste form by a factor of four. Since the use of fins adds substantially to the cost, cost studies need to be performed to establish economic viability.

10.4. Recommendations

a. A system engineering analysis of the solid waste storage canister should be carried out, to include all steps--procurement, filling, shipping, and storage at the reprocessing plant and the RSSF. Such an analysis should include definition of design options for containment, transfers, cooling, surveillance, quality control, etc.

The results of such an analysis would be a reference canister whose behavior in the waste handling environment would have been subjected to systematic examination at all stages and whose design would meet identified criteria according to presently available information. This analysis could be part of a systematic analysis of various options for high-level waste storage. The analysis should be sufficiently flexible to include consideration of (a) air *vs.* water cooling at the reprocessing plant and in shipment casks, (b) various cooling times at which operations (*e.g.*, liquid-to-solid conversion and shipment to the RSSF) are conducted, and (c) additional operations at appropriate cooling times to enhance reliability or to take advantage of the rapid decline in decay heat with time (*e.g.*, overpack addition prior to disposal, and repackaging in larger canisters at late stages).

b. Materials chemistry of the calcine-canister interaction for all operations involving the combination of these materials should be studied. Included in this work would be the properties of calcine and their relation to its history and composition, the chemistry of the canister material (corrosion), and migration of fission products in thermal gradients that affect corrosion. These properties and processes would be related to specific system design for reliable containment. This study would interface with work on solidification of wastes and post-solidification treatments. Similar studies are needed for the glass form. The results of this work would allow estimates of the reliability of containment of waste to be made where internal effects are critical.

c. Consideration should be given to modifying existing waste forms or developing new waste forms to yield compositions that are more stable (in the case of glass) or more conductive (in the case of calcine). Increased stability would remove possible doubts about corrosive effects attributable to long-term changes (*e.g.*, devitrification).

Methods of enhancing the long-term stability of glass by intentionally inducing crystallization by appropriate additives should be examined. Further, application to wastes of the body of technology that has been applied to the fabrication of more stable (in comparison to glass) commercial microcrystalline glass-ceramics should be considered.

d. There is increasing evidence that stainless steel (Type 304L) may not be the best canister material because of its susceptibility to stress-corrosion cracking. Systematic and practical corrosion studies should be conducted on alternative candidate materials that are based on the results of the systems analysis suggested above. These studies would allow the containment of waste to be estimated where external effects predominate.

e. Program items (a) to (d) listed above are complementary. It is not clear that the necessary work on each program has been established for high-reliability waste containment. Hence, we urge that such programs be funded and initiated to the fullest extent, starting as soon as possible.

APPENDIX A – REFERENCE HEAT LOADINGS AND CANISTER DIMENSIONS INCORPORATING VARIATION OF THERMAL CONDUCTIVITY WITH TEMPERATURE

In Section 3.7, heat loadings and canister dimensions were presented on the basis of reference thermal conductivities assumed to be constant with temperature. This was based on information obtained from ARHCO and PNL.

The calculations in Section 3.7 were repeated using a model that reflected variations in thermal conductivities with temperature.

A recent quarterly report[1] gives the thermal conductivity of PW-4b fluid-bed calcine as a function of temperature and density. The results (presented below) are not grossly different from those given in Section 3.7.

$$k = [0.177 + 0.1(\rho - 2.1)](1 + 0.00148T) \tag{1}$$

k is in $W/(m)(°C)$

ρ is in g/cm^3

T is in $°C$

Though the reference waste for this report does not conform exactly to the PW-4b composition, the relation shown in equation 1 was used to recalculate heat loadings and canister dimensions. The value of thermal conductivity used in Section 3.7 was 0.2 Btu/hr°F ft; using equation 1, the values (for $\rho = 2.0$) are 0.111 Btu/hr°F ft at 100°C and 0.182 Btu/hr°F ft at 600°C.

In the case of glass, the following relation was used.[2]

$$k[W/(m)(°C)] = 0.00095T\ [°C] + 0.75 \tag{2}$$

This relation yields values of thermal conductivities of 0.488 and 0.873 Btu/hr°F ft for 100 and 800°C, respectively. In Section 3.7, a value of 0.6 was used.

The results of the repeated calculations are shown in Tables A.1 (shipment in a water-cooled cask) and A.2 (shipment in an air-cooled cask). Figure A.1 was used in obtaining temperature information for the air-cooled case.

The revised information indicates that a slightly larger canister may be used for the glass waste form at one year's cooling (11.91 in. vs. 11.34 in.), and a slightly smaller canister for the calcine waste form (with fins) (6.44 in. vs. 7.61 in.). This is based on not exceeding centerline temperatures of 800°C in the case of glass, and 600°C in the case of calcine. If fins are not used, a cooling time of 3.5 years (was 2.5 years) is needed for calcine at the time of filling if a six-in. canister is to be used, and a cooling time of 6.3 years (was 4.1 years) is needed for a canister having waste capacity equivalent to that of glass.

TABLE A.1. Conditions of Shipment of Waste Forms with
Water Cooling at a Cooling Time of Ten Years[a]

Waste Form	Cooling Time at Filling (yr)	Waste Form Diameter, in.(cm)	Heat Rate (kW/ft^3)[b]		Shipping Temperatures,°F(°C)	
			At Filling	At Shipment	ΔT Across Waste Form	Waste Centerline
Glass	1	11.91 (30.2)	4.23	0.423	183 (102)	311 (155)
Calcine						
with fins	1	6.44 (16.4)	9.17	0.917	129 (72)	257 (125)
without fins	3.47[c]	6.0 (15.2)	2.64	0.917	407 (226)	535 (279)
without fins	6.31[d]	8.09 (20.5)	1.45	0.917	679 (377)	807 (430)

[a] See second footnote on page 12.

[b] To convert to kW/m^3, multiply by 35.3.

[c] Cooling time required to permit the use of 6-in. canisters.

[d] Cooling time required to allow use of canister having waste capacity equivalent to that for glass.

TABLE A.2. Conditions of Shipment of Waste Forms in a Dry Cask

Waste Form	Cooling Time at Filling (yr)	Cooling Time at Shipment (yr)	Heat Rate (kW/ft^3) [a]		Shipping Temperatures, °F(°C)		
			At Filling	At Shipment	Waste Centerline	Canister Wall	ΔT
Glass							
11.91 in.	1	10	4.23	0.423	851 (454)	716 (380)	135 (74)
Calcine							
6.44 in. with fins	1	10.4	9.17	0.88	1112 (600)	1037 (558)	75 (42)
6.00 in. with no fins	3.47[b]	14.9	2.64	0.61	1112 (600)	924 (495)	188 (104)
8.09 in. with no fins	6.31[c]	17.8	1.45	0.51	1112 (600)	819 (437)	293 (163)

[a] To convert to kW/m^3, multiply by 35.3.

[b] Cooling time required to permit the use of 6-in. canisters.

[c] Cooling time required to allow use of canister having waste capacity equivalent to that for glass.
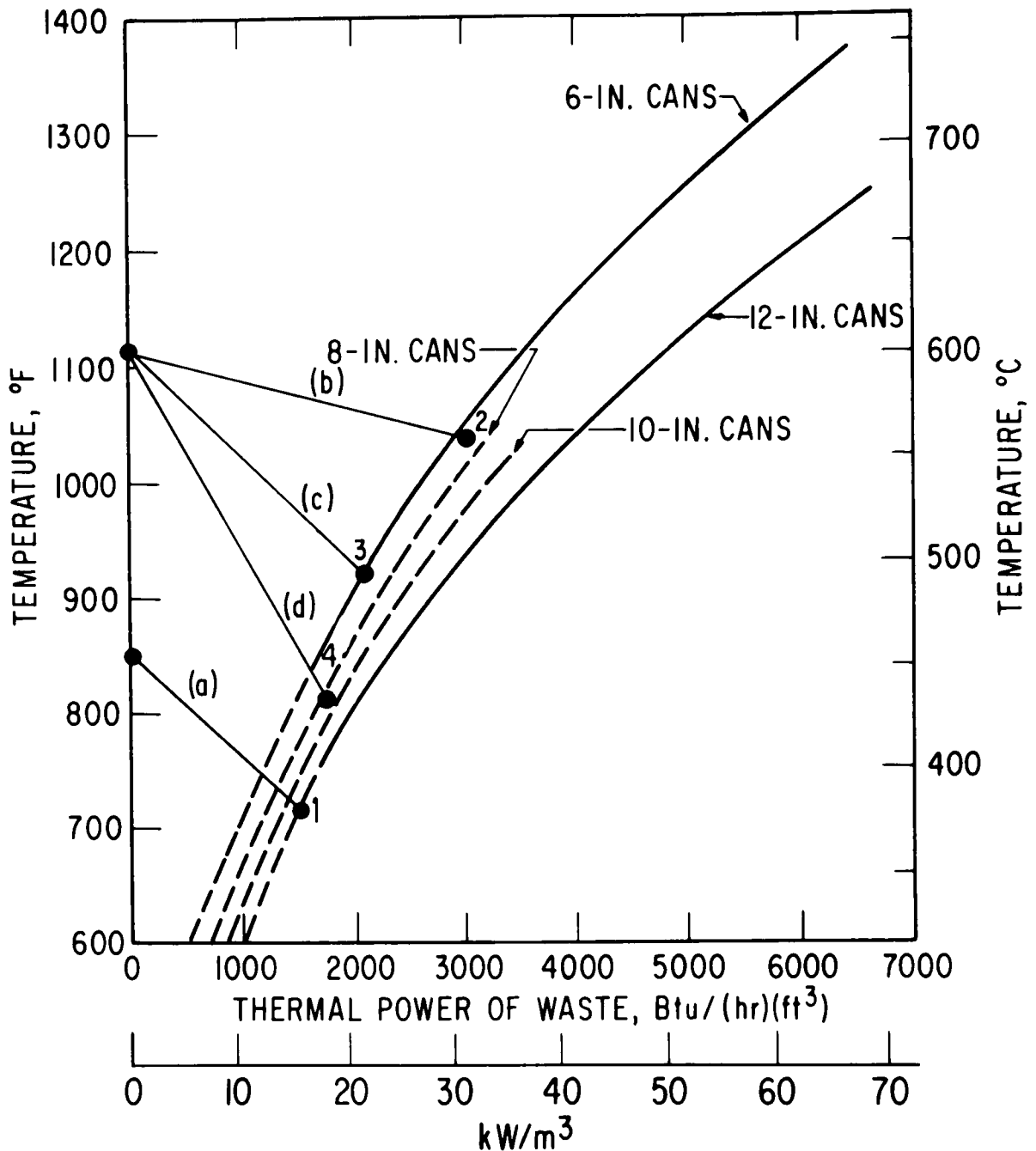
Fig. A.1. Surface Temperature of the Hottest Canister in a ∿100-Ton Dry Cask.
(dashed lines added for this report)

Terminal points of lines (a) through (d) show waste centerline temperatures
and canister wall temperatures.

(a) Glass in 11.91-in. canisters shipped after 10-yr cooling
(b) Calcine (with fins) shipped in 6.44-in. canisters after 10.4 yr cooling
(c) Calcine (no fins) shipped in 6-in. canisters after 14.9-yr cooling
(d) Calcine (no fins) shipped in 8.09-in. canisters after 17.8-yr cooling

At a cooling time of 10 years, all wastes can be shipped in a water-filled cask without exceeding waste temperatures limits.

None of the calcine forms can be shipped in air-cooled casks after 10 yr cooling. To meet centerline temperature limitations, the 6.4-in. canister with fins can be shipped after 10.4 yr. The 6.0- and 8.1-in. canisters without fins must be cooled 14.9 and 17.8 yr, respectively. In all cases considered for air-cooled shipments, canister wall temperatures are in excess of 700°F. Sensitization of stainless steel may well be expected at these temperatures.

References for Appendix A

1. J. L. McElroy (comp.), <u>Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, October through December 1974</u>, BNWL-1893, p. 43.

2. J. E. Mendel and J. L. McElroy, <u>Waste Solidification Program</u>, Vol. 10, Evaluation of Solidified Waste Products, BWNL-1666, p. 5.26 (July 1972).